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PART B
WATER QUALITY RESEARCH

NOVEMBER 30 &
DECEMBER 1, 1987

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PART B

WATER QUALITY RESEARCH

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INTRODUCTION

Environment Ontario holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario universities and by private research organizations and companies.

The papers presented at the 1987 Technology Transfer Conference are included in five volumes of Conference Proceedings corresponding to the following sessions:

Part A:	Air Quality Research
Part B:	Water Quality Research
Part C:	Liquid & Solid Waste Research
Part D:	Analytical Methods
Part E:	Environmental Economics.

This part is a compilation of papers presented during Session A of the Conference.

For further information on any of the papers, the reader is kindly referred to the authors or to the Research Management Office at (416) 323-4574, 332-4573.

ACKNOWLEDGMENTS

The Conference Committee would like to thank the authors for their valuable contributions to environmental research in Ontario.

DISCLAIMER

The views and ideas expressed in these papers are those of the authors and do not necessarily reflect the views and policies of Environment Ontario, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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MONITORING OF ORGANIC CONTAMINANTS USING FRESHWATER MUSSELS

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D.Haffner*, P. Hebert

Great Lakes Institute,
University of Windsor,
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N9B 3P4

INTRODUCTION

Water quality studies have evolved from spot check collections towards more thorough ecological assessments. A major component of this process is the development of biomonitoring techniques. Originally, biomonitoring was human health related (assessment of coliform levels, pathogenic bacteria and viruses), but gradually became associated with the concept of measuring and monitoring ecosystem health. Presently biomonitoring techniques are being used as water surrogates, indicators of stress and as a means to manage renewable resources. The use of biological tools as a surrogate of water measurements is very prevalent today with the need to set and monitor guidelines for protecting human and environmental health. Hydrological variability, combined with low concentrations, tends to make water a very difficult medium to monitor. When monitoring trace organics in water, frequently non-detectable results are encountered, and these non-detection levels are regarded more as an analytical handicap than as an accurate determination of the presence or levels of organics in the aquatic environment.

A potentially more sensitive mechanism to determine the presence and levels of trace organics is the use of biological monitors. The key phrase usually associated with such an approach is that the organisms act as environmental integrators. There have been, however, very few studies to assess what is actually being integrated. The spatial and temporal scales of variability existing in either the body burden or response of an organism to trace organics are usually unknown.

To answer such questions is essential if biomonitoring is to become a routine tool of water quality management programs. The answer requires research into aspects of habitat selection and utilization. The determination of the sensitivity of organisms to compounds of concern must include the physiological status of the organisms and the interaction of life cycles and exposure patterns. Because of the complexity of factors that can regulate an organisms response, biomonitoring techniques must be focussed on biota that have simple life cycles and are generalists with respect to habitat utilization. A preferred organism would also be able to tolerate the stress of handling for experimental purposes, and not deviate for long periods from a physiological 'norm'. An organism which is generally accepted to meet these conditions is the freshwater mussel.

The following study focussed on the measurement of *in vitro* uptake and depuration rates of trace organics by freshwater mussels. Exposures were designed to test whether water or sediment were the main source of contaminants, and to measure seasonal uptake rates until equilibrium conditions were obtained.

MATERIALS and METHODS

Mussel collection and deployment

Elliptio complanata individuals were obtained from Balsam Lake, a pristine lake located near Lindsay, Ontario. For the depuration study, *Lampsilis radiata* specimens were collected by diver from a contaminated site in Lake St. Clair (Fig. 1). Mussels from this locale contain relatively high concentrations of contaminants (Pugsley *et al.*, 1985). The mussels ranged in size from 6.5 to 7.2 cm and 6.5 to 7.5 cm for *E. complanata* and *L. radiata* respectively, representing ages of approximately eight to ten years.

Lampsilis radiata is an indigenous species that has a wide distribution in the lakes and rivers of southern Canada (Clarke, 1981). *Elliptio complanata* has been widely used by the Ministry of the Environment (Kauss *et al.*,1981, Kauss and Hamdy, 1985), but is not native to the Lake Huron-Lake Erie connecting channel.

After collection, mussels were transported in bags of lake water at 10° C and held in chilled tanks until their deployment. At the conclusion of an experiment, specimens were immediately shucked, allowing excess fluid to drain, and wrapped in hexane-rinsed aluminum foil. Samples were frozen at -50° C until analyzed, on average three weeks after collection. Shells were measured (length) and identified following Clarke (1981).

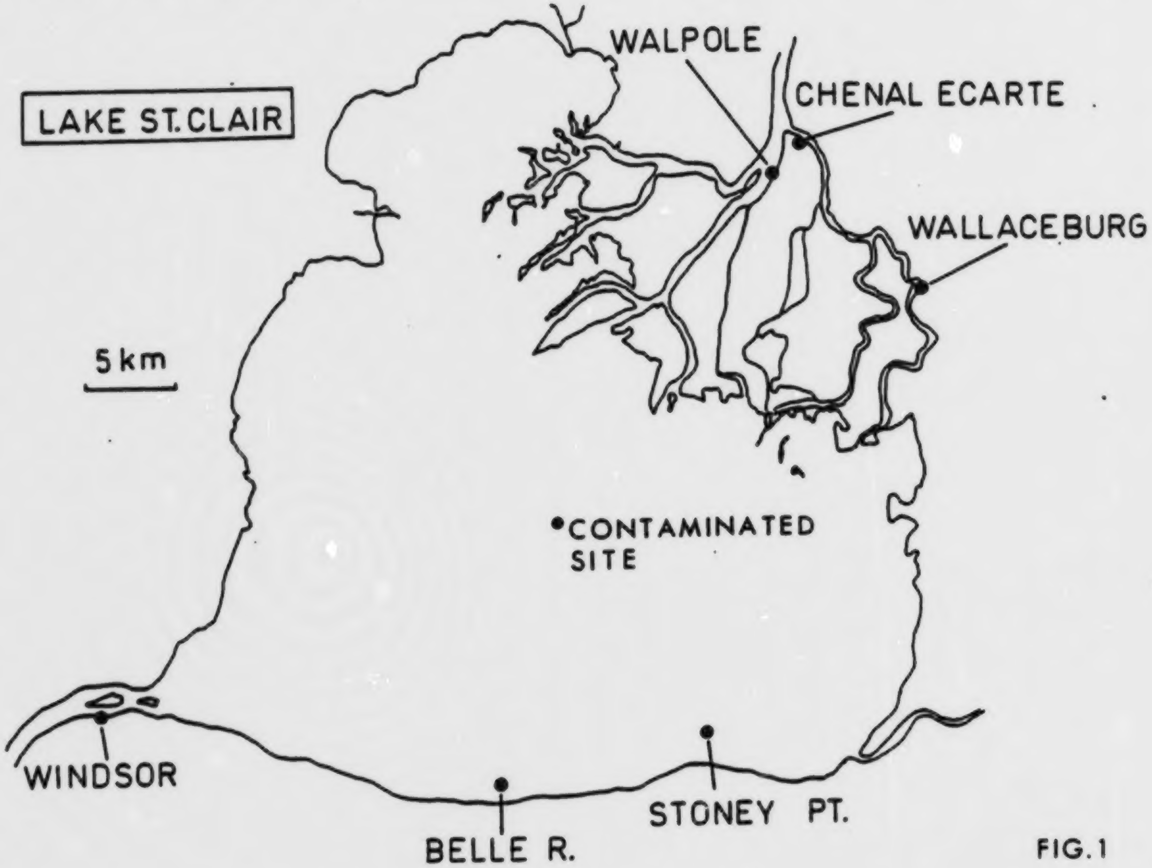

LAKE ST. CLAIR
WALPOLE
CHENAL ECARTE
WALLACEBURG
5 km
CONTAMINATED SITE
WINDSOR
BELLE R.
STONEY PT.

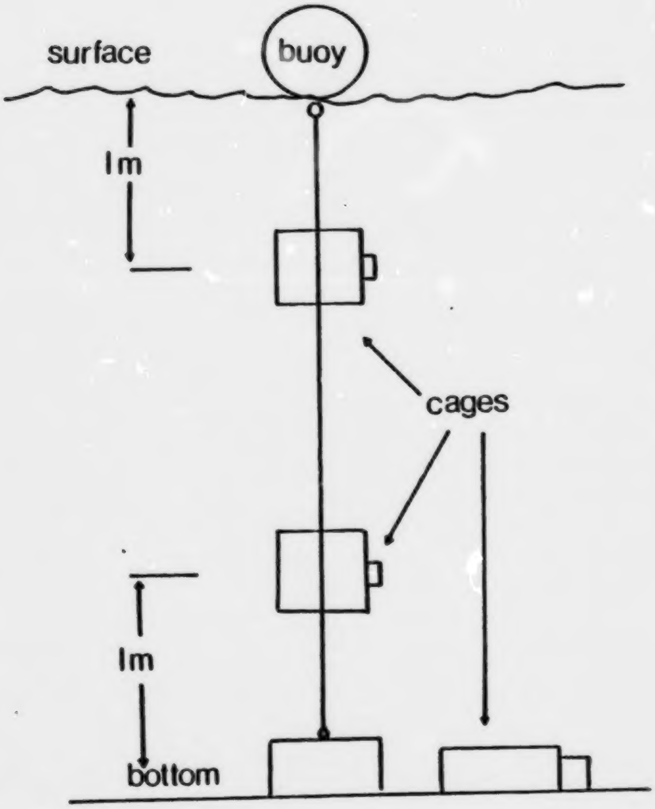
FIG. 1

Accumulation of contaminants

Elliptio complanata individuals placed in wire-mesh 'pillow' cages, as used by Kauss and Hamdy (1985), were exposed for 20-86 days at five sites in the St. Clair River and Lake St. Clair (Walpole, Chenal Ecarte, Wallaceburg, Stoney Point, Belle River) (Fig. 1). The mussels were suspended near the surface ('top cage') as well as on the sediment ('sed cage') (Fig. 2). An additional cage, approximately one m from the sediment-water interface ('bottom cage') was suspended at the Walpole and Chenal Ecarte sites. Mortality was generally less than one percent except for the Walpole sediment cage where ten of the twenty-two mussels deployed died. Three exposed individuals were replaced with three uncontaminated mussels at approximately twenty day intervals. The deployment and recovery schedule is outlined in Fig. 3. At least three specimens for a given exposure period from each site were analyzed, representing a total of 204 mussels. The sediment cage at Chenal Ecarte was disturbed resulting in no data for the first four exposure periods.

Depuration of contaminants

To study the pattern of contaminant purging, seventy L. radiata specimens were transplanted from a contaminated site in Lake St. Clair (Fig. 1) to a site two km south of the head of the St. Clair River on 4 September 1986. This location is upstream of the industrialized sections of the river. To monitor the level of


surface
buoy
Im
cages
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bottom

Figure 2 Method used to deploy mussel cages.

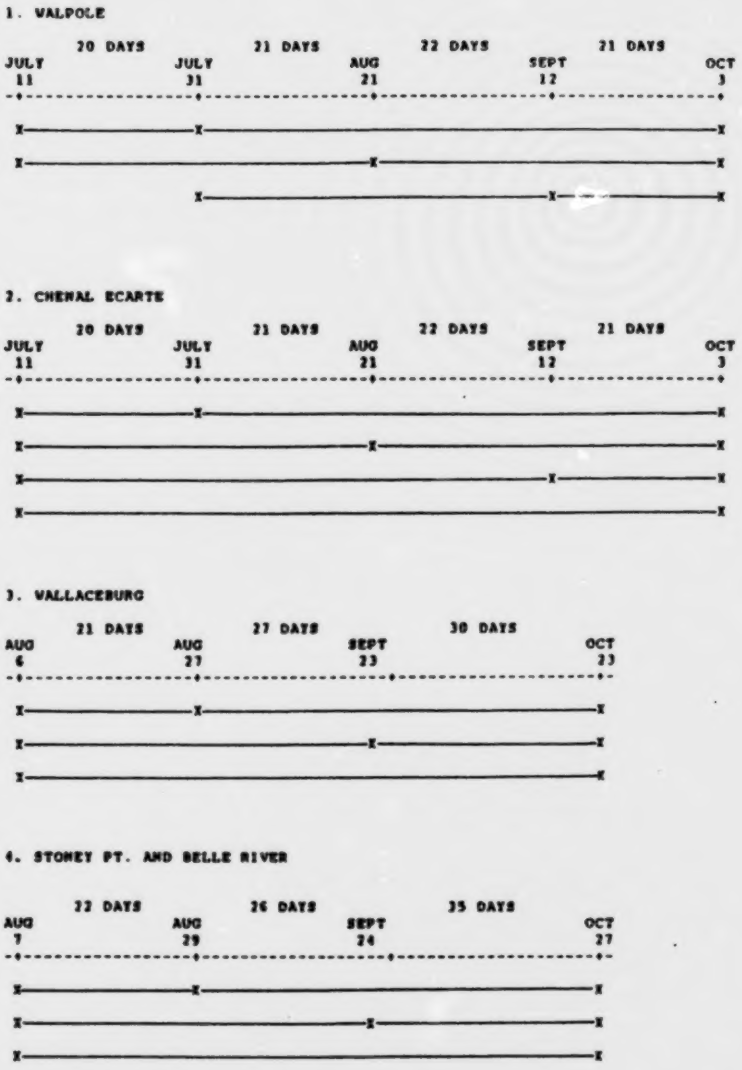
1. WALPOLE
20 DAYS
21 DAYS
22 DAYS
21 DAYS
JULY 11
JULY 31
AUG 21
SEPT 12
OCT 3
2. CHENAL ECARTE
20 DAYS
21 DAYS
22 DAYS
21 DAYS
JULY 11
JULY 31
AUG 21
SEPT 12
OCT 3
3. WALLACEBURG
21 DAYS
27 DAYS
30 DAYS
AUG 6
AUG 27
SEPT 23
OCT 23
4. STONEY PT. AND BELLE RIVER
22 DAYS
26 DAYS
35 DAYS
AUG 7
AUG 29
SEPT 24
OCT 27

Fig 3. Deployment and recovery schedule for the five sites. Three mussels were deployed and collected on the days indicated (x).

contaminants at the purging site, thirty uncontaminated E. complanata were also deployed. All specimens were kept in four pillow cages, containing approximately 25 organisms each. Ten individuals of L. radiata were removed after exposure periods of 4, 8, 15, 22, 35, and 59 days. Control mussels (E. complanata, N = 6) were sampled after 22 and 59 days.

Analysis for organic contaminants

Analysis was performed in the Great Lakes Institute organics laboratory, University of Windsor, Windsor, Ontario.

All glassware was washed with hot, soapy water (Contrad 70, Canlab) and rinsed well with hot water. Immediately prior to use, glassware was rinsed in succession with three portions of acetone, three portions of petroleum ether, and a final rinse of pesticide-grade hexane. All solvents that were in direct contact with the samples were of pesticide grade.

Mussel tissue was thawed and some gill tissue was removed for sex determination. The remaining tissue was weighed and then ground with a Polytron homogenizer for 90 s in 120 ml acetonitrile and 40 ml distilled water. The homogenate was filtered with suction through a sintered glass funnel, followed by a second homogenization with 50 ml acetonitrile and rinsing with two 20 ml portions of acetonitrile.

The combined filtrates were extracted with 300 ml petroleum ether in three portions; 150 ml, 75 ml, and 75 ml. One ml concentrated sulphuric acid was added to the initial extraction to hydrolyze lipids. The combined petroleum ether extracts were washed with 200 ml distilled water and dried by passage through 20 mm x 40 cm glass columns containing 15 g anhydrous sodium sulphate. The dried extracts were concentrated to 5 ml with a Kuderna-Danish evaporator and passed through columns with 30 g florisil under 8 g anhydrous sodium sulphate. The column was eluted with 200 ml of petroleum ether, which was concentrated again to 5 ml. The concentrate was diluted to 10 ml with hexane, of which 1.0 ul was injected into a gas chromatograph.

A Hewlett-Packard 5790A capillary column gas chromatograph with an electron-capture detector fitted with a 30 m x 0.25 mm fused silica column containing a cross-linked DB-5 stationary phase (J & W Scientific) and in combination with a 7671 auto-injector and a 3390A integrator was used for analysis. The following conditions were employed:

Injector temperature: 250° C
Column temperature programing: 0.5 min at 50° C, 50-250° C at 2° C per min, 20.0 min at 250° C
Detector temperature: 300° C
Carrier gas: helium at 1.5 ml per min
Detector make-up gas: 5% methane/95% argon at 60 ml per min
Injection mode: splitless

Samples were analyzed for pentachlorobenzene (QCB), hexachlorobenzene (HCB), octachlorostyrene (OCS), and polychlorinated biphenyls (PCBs). Quantification of the compounds was performed by comparing peak areas against a set of standards containing known concentrations. The data for PCBs are in the process of being summarized and thus are not presented here. Individual congeners were chosen as the method of representing PCBS as oppose to Aroclors due to inaccuracies encountered when assuming that the composition of the Aroclor is similar in both the environmental sample and the standard mixture. Difficulty exists in comparing values presented as 'Total PCBs' or a specific Aroclor because of variation in the methods of quantification. An Aroclor contains approximately 60 PCB congeners, each of which has specific chemical properties that determine its behaviour in the environment. The trend towards reporting PCBs as individual congeners will greatly enhance the ecological significance of the information obtained (Duinker et al., 1980, Schwartz et al., 1987).

The limit of quantification for QCB, HCB and OCS was 0.2 ppb and 0.5 ppb for individual PCB congeners. Recovery efficiencies were estimated by adding known quantities of compounds to uncontaminated mussel tissue and solvents. Recovery values for mussel tissues were 87 percent for OCS and PCB congener 180, and 89, 93, and 94 percent for congener 110, HCB, and QCB respectively. Solvent contaminant recoveries ranged from 77 percent to 95 percent. No corrections were made for the recovery. All chromatographs were visually inspected before data summary. Concentrations were ordinarily determined by comparing integrated peak values with those of a standard of a known concentration. In a few cases, the integrator failed to report an area for a peak that had exceeded the baseline. In such cases the peak area was estimated by comparisons with reported peaks of a similar size. An approximation of the positive peak area was made when the peak, as defined by the integrator, clearly had penetrated or failed to reach the baseline.

Each set of five samples was accompanied by a solvent blank, subjected to the entire extraction procedure, to check the cleanliness of glassware and reagent purity. A standard was also ran for each five sample set to account for changes in machine sensitivity.

All concentrations are expressed as parts per billion (ppb) and are based on wet weights of tissues. The mean water content of twelve E. complanata specimens was 89 percent (S.E. = .003). Thus body burdens can be expressed on a dry weight basis using a conversion factor of 9.09. This is greater than the multiplication factors of 6.25 and 6.67 given by Kauss and Hamdy (1985) and Pugsley et al. (1985), respectively. Lipid concentrations (expressed as percent of dry weight) were determined by extraction with petroleum ether and heating at 120° C for 24 hr. Lipid content of E. complanata ranged from 1.8 to 3.4 percent (mean = 0.026, S.E. = .005, N = 15). Kauss and Hamdy (1985) found lipid content in E. complanata to vary between 0.7 and 1.9 percent of wet weight. Values may be expressed on a lipid basis by multiplying dry weight concentrations by 38.5. As a result of the spatial and seasonal variation in lipid content which may occur among individuals due to the effects of reproduction, sex, and age, it might be necessary to obtain lipid concentrations for every specimen (Boon et al., 1985) even though the lipid content is so low (de Kock, 1983, Gardner, pers. comm., Hartley and Johnston, 1983).

Statistical analysis

Two-way factorial ANOVAs with replication were used to analyze for differences in body burdens among cage position, exposure periods, and sites. The ANOVAs were computed using the Systat computer package. Analysis of purging data for differences of means and deviation from linear regression (expressed as test for linear regression) followed Sokal and Rohlf (1969). The confidence intervals used represent two standard errors.

RESULTS

ACCUMULATION

Differences in body burden among depths

There were no significant differences in the body burdens of QCB, HCB, and OCS in mussels placed in cages near the surface, one m from the sediment, and on the sediment at the Walpole and Chenal Ecarte sites with the exception of QCB at Chenal Ecarte (Tables 1, 2, Figs 4, 5). For six exposure periods there were no significant differences in the body burdens of the study compounds in mussels placed near the surface and one m from the sediment at Walpole and Chenal Ecarte (Tables 3, 4). At Wallaceburg, no significant differences were detected in the body burdens of QCB, HCB, and OCS in mussels placed in cages near the surface and those deployed on the sediment (Table 5, Fig 6).

Contaminant accumulation at each site

Although the accumulation of each contaminant was similar at all depths within a site, there were differences in the pattern of contaminant uptake among the three compounds investigated. For example, OCS displayed a relatively linear increase in concentration with increased exposure time at Walpole, Chenal Ecarte, and Wallaceburg with detectable concentrations observed after twenty days (Figs 4, 5, 6). The levels of HCB were also detectable after twenty days and continued to increase with greater exposure time, though the accumulation profile was more

Table 1. Summary of a two-way (three depths (top, bottom, and sediment) and three exposure periods (7/31 - 9/12, 7/31 - 10/3, 8/21 - 10/3)) ANOVA comparing QCB, HCB, and OCS accumulation at the Walpole site.

Contaminant	Source of variation	df	MS	F	P
QCB	Depth	2	0.048	1.75	ns
	Exposure	2	0.085	3.12	ns
	Interaction	4	0.027	1.00	ns
	Error	29	0.027		
HCB	Depth	2	0.697	1.09	ns
	Exposure	2	6.739	10.52	<.001
	Interaction	4	0.620	0.97	ns
	Error	29	0.641		
OCS	Depth	2	1.324	0.17	ns
	Exposure	2	214.477	27.92	<.001
	Interaction	4	16.840	2.19	ns
	Error	29	7.683		

Table 2. Summary of a two-way (three depths (top, bottom, and sediment) and three exposure periods (7/31 - 10/3, 8/21 - 10/3, 9/12 - 10/3)) ANOVA comparing QCB, HCB, and OCS accumulation at the Chenal Ecarte site.

Contaminant	Source of variation	df	MS	F	P
QCB	Depth	2	0.294	3.64	<.05
	Exposure	2	0.105	1.03	ns
	Interaction	4	0.120	1.49	ns
	Error	29	0.081		
HCB	Depth	2	2.138	1.59	ns
	Exposure	2	6.977	5.20	<.05
	Interaction	4	2.569	1.91	ns
	Error	29	1.343		
OCS	Depth	2	19.709	1.23	ns
	Exposure	2	166.230	10.33	<.001
	Interaction	4	18.396	1.14	ns
	Error	29	16.090		

Fig 4. Mean accumulation of QCB, HCB, and OCS at the Walpole site for *Elliptio complanata* mussels (n = 3) exposed at three depths. Outer symbols represent ± 1 standard error.

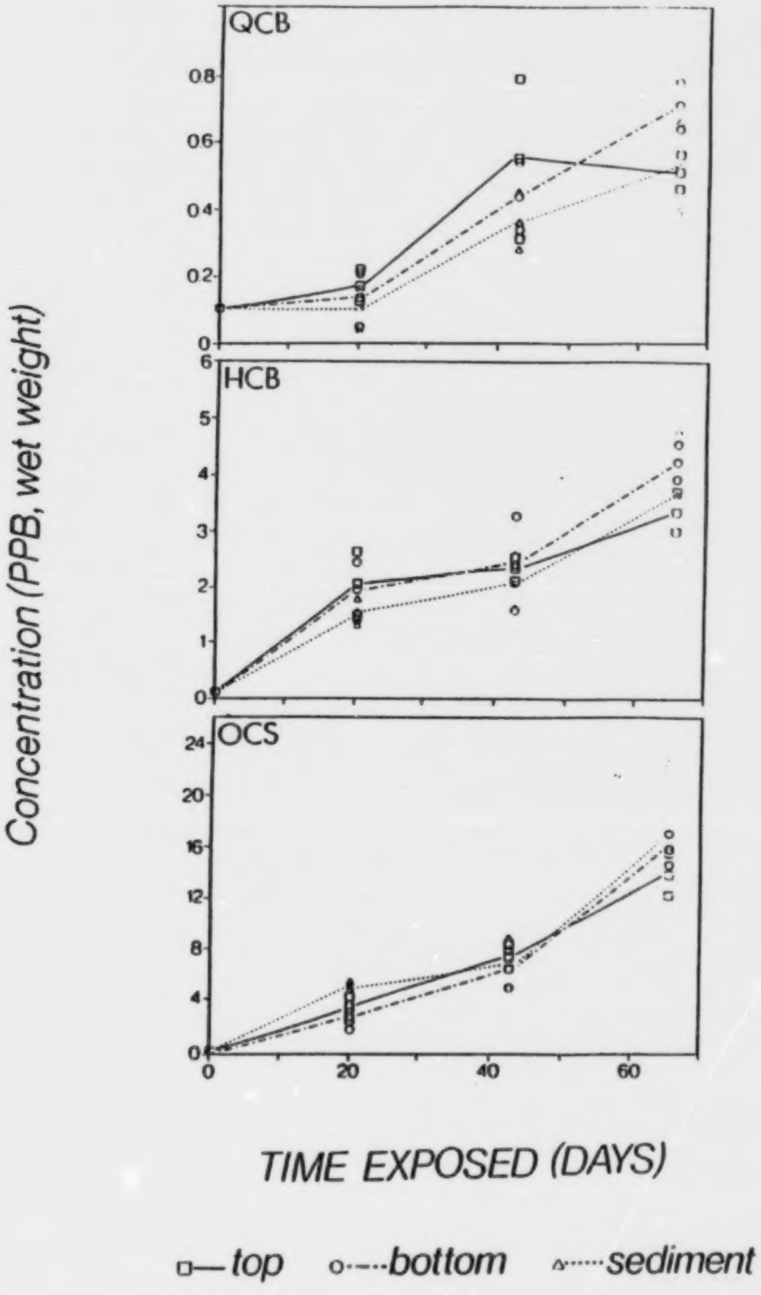
QCB
0.8
0.6
0.4
0.2
0
HCB
6
5
4
3
2
1
0
OCS
24
20
16
12
8
4
0
0
20
40
60
Concentration (PPB, wet weight)
TIME EXPOSED (DAYS)
□— top
○-·-·bottom
△····sediment

FIG. 4

Fig 5. Mean accumulation of QCB, HCB, and OCS at the Chenal Ecarte site for *Elliptio complanata* mussels (n = 3) exposed at three depths. Outer symbols represent ± 1 standard error.

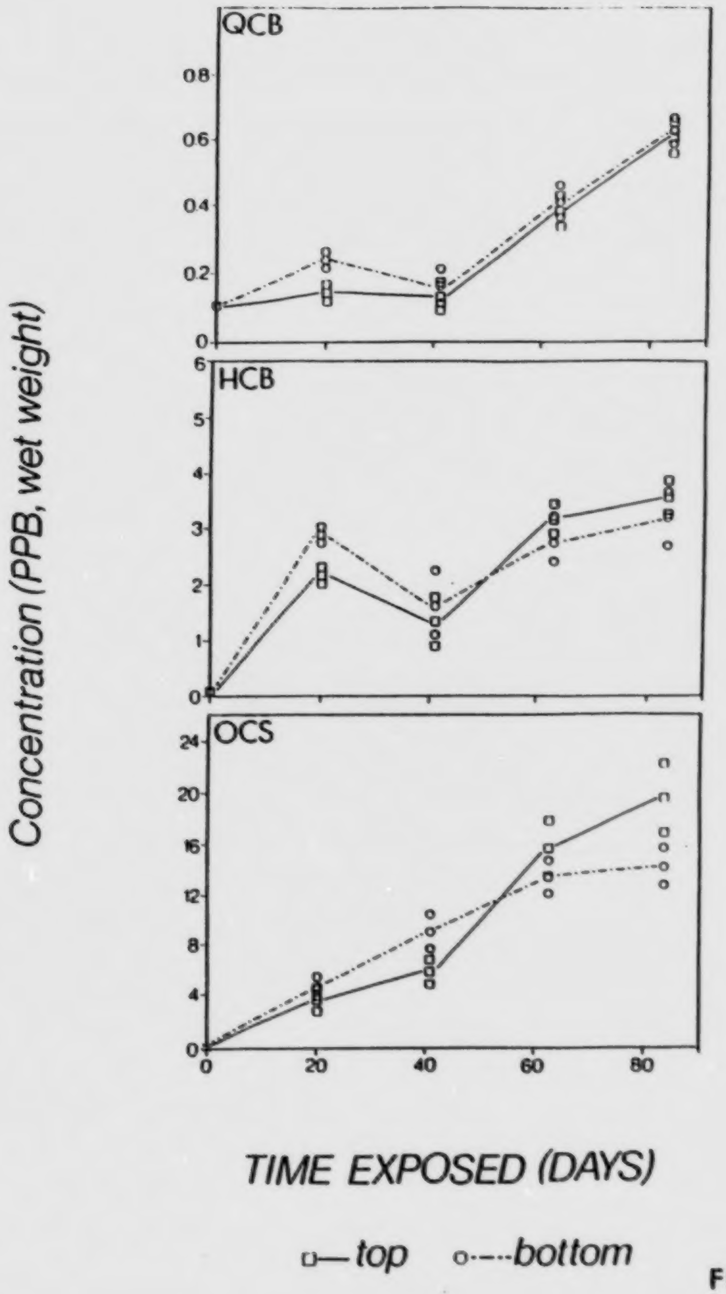
QCB
0.8
0.6
0.4
0.2
0
HCB
6
5
4
3
2
1
0
OCS
24
20
16
12
8
4
0
0
20
40
60
80
Concentration (PPB, wet weight)
TIME EXPOSED (DAYS)
□— top
○-·-·bottom

FIG. 5

Table 3. Summary of a two-way (two depths (top and bottom) and six exposure periods (7/11 - 7/31, 7/11 - 8/21, 7/31 - 9/12, 7/31 - 10/3, 8/21 - 10/3, 9/12 - 10/3)) ANOVA comparing QCB, HCB, and OCS accumulation at the Walpole site.

Contaminant	Source of variation	df	MS	F	P
QCB	Depth	1	0.005	0.26	ns
	Exposure	5	0.407	19.73	<.001
	Interaction	5	0.027	1.33	ns
	Error	34	0.021		
HCB	Depth	1	0.010	0.02	ns
	Exposure	5	6.923	11.56	<.001
	Interaction	5	0.740	1.24	ns
	Error	34	0.599		
OCS	Depth	1	0.484	0.08	ns
	Exposure	5	213.335	35.42	<.001
	Interaction	5	6.633	1.10	ns
	Error	34	6.023		

Table 4. Summary of a two-way (two depths (top and bottom) and seven exposure periods (7/11 - 7/31, 7/11 - 8/21, 7/11 -9/12, 7/11 - 10/3, 7/31 - 10/3, 8/21 - 10/3, 9/12 - 10/3)) ANOVA comparing QCB, HCB, and OCS accumulation at the Chenal Ecarte site.

Contaminant	Source of variation	df	MS	F	P
QCB	Depth	1	0.000	0.00	ns
	Exposure	6	0.452	7.35	<.001
	Interaction	6	0.050	0.81	ns
	Error	33	0.061		
HCB	Depth	1	0.759	0.75	ns
	Exposure	6	10.366	10.18	<.001
	Interaction	6	0.629	0.61	ns
	Error	33	1.018		
OCS	Depth	1	8.525	0.96	ns
	Exposure	6	125.233	14.07	<.001
	Interaction	6	12.765	1.43	ns
	Error	33	8.903		

Table 5. Summary of a two-way (two depths (top and sediment) and five exposure periods (8/6 - 8/27, 8/6 - 9/23, 8/6 - 10/23, 8/27 - 10/3, 9/23 - 10/23)) ANOVA comparing QCB, HCB, and OCS accumulation at the Wallaceburg site.

Contaminant	Source of variation	df	MS	F	P
QCB	Depth	1	0.013	0.82	ns
	Exposure	4	0.568	36.95	<.001
	Interaction	4	0.005	0.33	ns
	Error	33	0.015		
HCB	Depth	1	0.294	0.26	ns
	Exposure	4	10.533	9.29	<.001
	Interaction	4	0.578	0.51	ns
	Error	33	1.133		
OCS	Depth	1	3.240	0.33	ns
	Exposure	4	193.425	19.82	<.001
	Interaction	4	17.462	1.79	ns
	Error	33	9.762		

Fig 6. Mean accumulation of QCB, HCB, and OCS at the Wallaceburg site for *Elliptio complanata* mussels (n = 3) exposed at two depths. Outer symbols represent ± 1 standard error.

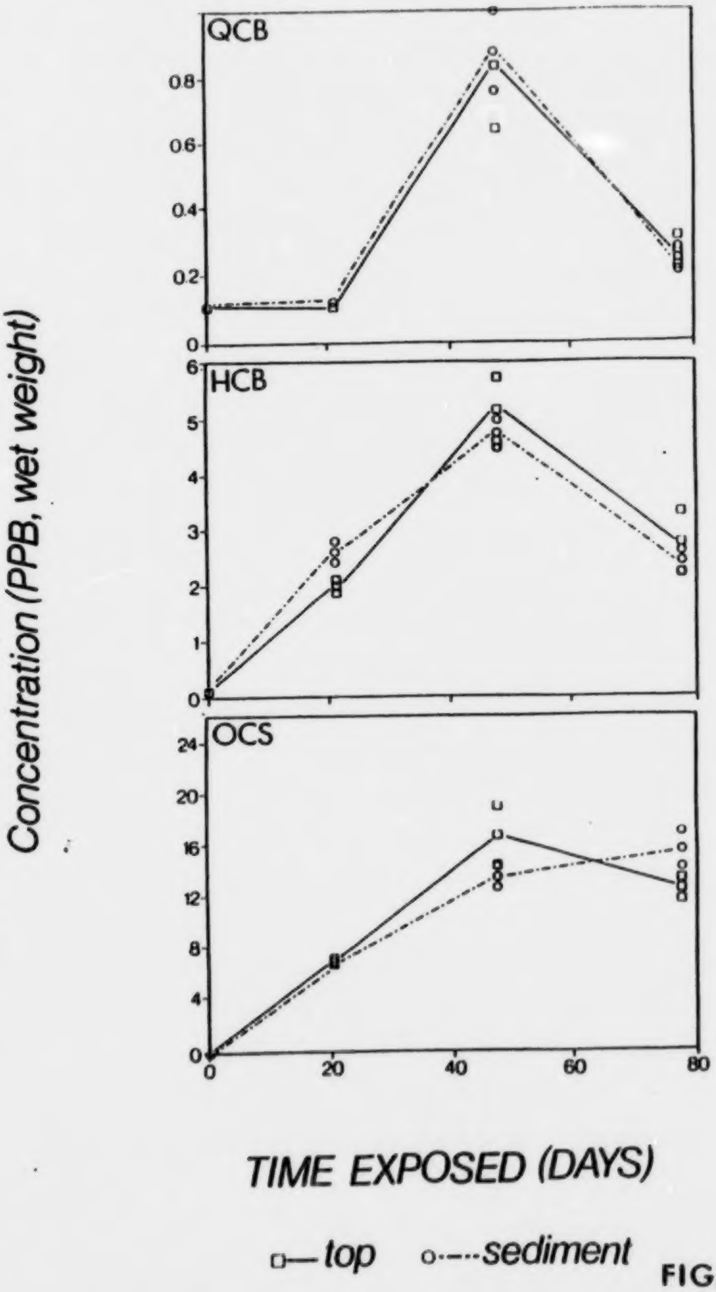
QCB
0
0.2
0.4
0.6
0.8
HCB
0
1
2
3
4
5
6
OCS
0
4
8
12
16
20
24
0
20
40
60
80
Concentration (PPB, wet weight)
TIME EXPOSED (DAYS)
□— top
○-·-·-sediment

FIG.6

erratic. At each site, body burdens of OCS were greater than those of HCB. Levels of QCB accumulated much more slowly with significant accumulation occurring after forty days and body burdens remaining much lower than those of HCB or OCS throughout the study (Figs 4, 5, 6).

The mean body burdens of the three contaminants declined after 48 days at the Wallaceburg site with the exception of OCS levels in mussels placed near the surface. The only other detected decrease in mean concentrations with a longer exposure period was for QCB in the surface mussels at Walpole.

There were significant differences in the body burdens among exposure times for all contaminants at Walpole, Chenal Ecarte, and Wallaceburg except QCB levels did not differ significantly among the six exposure periods at Chenal Ecarte.

No significant interactions were observed in any of the ANOVAs used to analyze the effects of cage location and site on contaminant uptake indicating that the concentration of contaminant accumulating for a given exposure period did not differ among the cages.

Variation in contaminant accumulation among sites

No significant differences were observed in the levels of QCB and OCS between the Walpole and Chenal Ecarte sites for seven exposure periods (Table 6). Concentrations of HCB were significantly greater at Chenal Ecarte than Walpole. Most of the variation observed was due to variation in body burdens among the

Table 6. Summary of a two-way ANOVA comparing QCB, HCB, and OCS levels between Walpole and Chenal Ecarte sites for seven exposure periods (7/11 - 7/31, 7/11 - 8/21, 7/31 - 10/3, 8/21 - 10/3, 9/12 - 10/3, 7/31 - 8/21, 7/31 - 9/12).

Contaminant	Source of variation	df	MS	F	P
QCB	Site	1	0.023	0.52	ns
	Exposure	6	0.832	18.94	<.001
	Interaction	6	0.014	0.32	ns
	Error	100	0.044		
HCB	Depth	1	4.329	4.89	<.05
	Exposure	6	17.843	20.14	<.001
	Interaction	6	0.963	1.09	ns
	Error	100	0.886		
OCS	Depth	1	22.740	2.21	ns
	Exposure	6	391.228	37.99	<.001
	Interaction	6	1.293	0.13	ns
	Error	100	10.300		

exposure periods (Table 6). The lack of significant interaction between exposure period and site for each contaminant suggests that the level of contaminant acquisition was similar for a given exposure period between the two sites.

Comparisons between the Wallaceburg and Walpole and Chenal Ecarte sites could not be made directly since the Wallaceburg site differed for both the season and length of exposure. However, QCB, HCB, and OCS accumulation at Wallaceburg was similar to the levels of uptake observed at Walpole and Chenal Ecarte (Figs 4, 5, and 6). Accumulation of all three contaminants was much lower at the Lake St. Clair sites of Stoney Point and Belle River than at sites in and adjacent to the St. Clair River (Table 7). After 81 days of exposure, the mean body burdens of QCB, HCB, and OCS in the mussels at the Lake St. Clair sites were less than one ppb.

Seasonal variation in contaminant accumulation

The mussel deployment and recovery schedule allowed for a comparison of contaminant accumulation between exposures of the same length but at different periods of the summer and fall. The pooled (all cages combined) mean body burdens for all three contaminants differed significantly among the starting dates for twenty and 41 day exposure periods at both the Walpole and Chenal Ecarte sites (Tables 8, 9). In all cases the latest starting date produced the greatest accumulation of contaminants for similar exposure times.

Table 7. Pooled mean body burdens (1 S. E.) for *Elliptio complanata* individuals exposed near the surface and on the sediment at Stoney Point and Belle River.

		Stoney Point				Belle River			
		Concentration (ppb, wet weight)							
Exposure Period	Days Exposed	N	QCB	HCB	OCS	N	QCB	HCB	OCS
8/7 - 8/29	22	6	0.10 (0.00)	0.29 (0.24)	0.17 (0.01)	6	0.10 (0.00)	0.41 (0.06)	0.24 (0.03)
8/7 - 9/24	48	6	0.13 (0.03)	0.38 (0.06)	0.53 (0.21)	6	0.35 (0.06)	0.32 (0.03)	0.42 (0.07)
8/7 - 10/27	81	5	0.32 (0.07)	0.77 (0.55)	0.19 (0.02)	5	0.26 (0.04)	0.22 (0.04)	0.22 (0.01)

Table 8. Seasonal variation in accumulation of contaminants at the Walpole site. Mean body burdens (1 S. E.) represent individuals pooled from all three cage positions. Tests are for significant differences among starting dates.

Days of Exposure	Starting Date	N	Conc. (ppb Wet Weight)		
			QCB	HCB	OCS
20	July 11	6	0.15(0.03)	1.99(0.34)	3.05(0.55)
20	July 31	3	0.09(0.03)	1.51(0.23)	5.02(0.33)
21	Sept 12	5	0.55(0.06)	3.10(0.29)	7.16(1.60)
Significance			***	*	*
41	July 11	6	0.12(0.02)	1.83(0.30)	6.60(1.20)
43	July 31	9	0.45(0.09)	2.31(0.29)	6.92(0.76)
43	Aug 21	16	0.63(0.03)	3.75(0.19)	14.47(0.67)
Significance			***	***	***

* $p < 0.05$ *** $p < 0.001$

Table 9. Seasonal variation in accumulation of contaminants at the Chenal Ecarte site. Mean body burdens (1 S. E.) represent individuals pooled from all three cage positions. Tests are for significant differences among starting dates.

Days of Exposure	Starting Date	N	Conc. (ppb Wet Weight) QCB	HCB	OCS
20	July 11	6	0.18(0.03)	2.48(0.17)	4.16(0.47)
20	July 31	3	0.23(0.10)	1.83(0.19)	4.60(0.83)
21	Sept 12	9	0.56(0.11)	3.48(0.36)	8.80(1.53)
Significance			*	*	*
41	July 11	6	0.15(0.03)	1.49(0.33)	7.50(1.04)
43	July 31	3	0.36(0.04)	3.00(0.27)	8.79(0.49)
43	Aug 21	19	0.73(0.07)	4.13(0.19)	15.22(0.86)
Significance			***	***	***

* $p < 0.05$ *** $p < 0.001$

DEPURATION

Pattern of contaminant loss

Lampsilis radiata specimens transferred from the contaminant plume in Lake St. Clair to a pristine site on the Upper St. Clair River displayed chemical specific purging rates and patterns (Table 10). More than two-thirds of the HCB body burden was purged during the first exposure period (4 days) and greater than 90 percent of the burden was lost within sixty days (Fig. 7). There were no significant losses of OCS initially, until the third sampling date, after which purging occurred through the remainder of the study (Fig 8). There were significant differences among the means for all contaminants among sampling periods (Table 10). Concentrations of HCB and OCS increased between the second and third sampling periods. As the ten mussels involved were analyzed on seven different days and in conjunction with mussels from Lake St. Clair and the first sampling it is unlikely that this increase was due to an analytical bias. Furthermore, three samples that clearly had the greater body burdens were processed at separate times.

After logarithmic transformation of the data, OCS displayed a linear purging pattern while the purging rate of HCB was clearly non-linear (Table 11).

Table 10. Mean percent loss (gain) of initial body burden in *Lampsilis radiata* after exposure at a pristine site in the Upper St. Clair River. Tests (@=.01) for differences among means for all sampling periods followed Sokal and Rohlf (1969).

Contaminant	Time since transfer (days)			Diff. among exposure means	
	4	8	59	F-ratio	Sig
HCB	67.8	72.4	90.2	48.89	Yes
OCS	25.5	16.9	58.2	6.06	Yes

Fig 7. Mean body burdens of HCB in *Lampsilis radiata* individuals transferred from site three in Lake St. Clair to the Upper St. Clair River and exposed for 59 days (n =10). Triangles represent the mean body burden of *Elliptio complanata* specimens transferred from Balsam Lake to the purging site.

PURGING of HCB

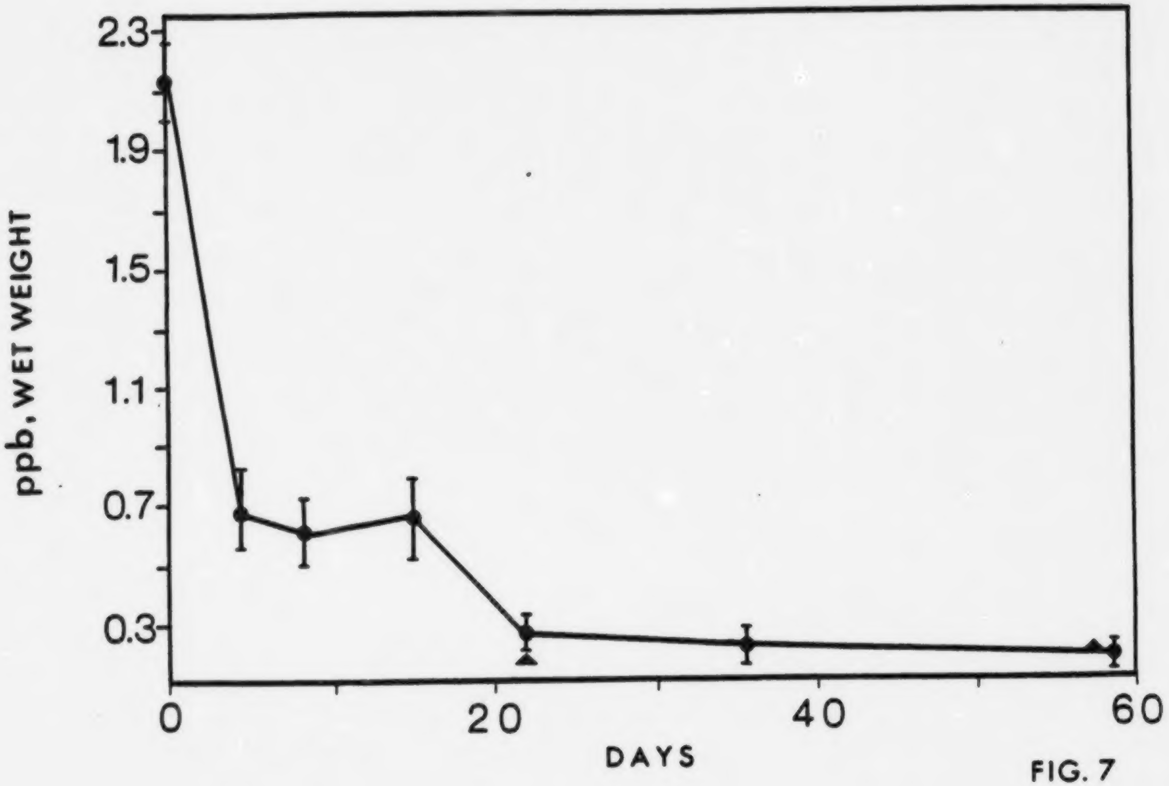

FIG. 7

Fig 8. Mean body burdens of OCS in *Lampsilis radiata* individuals transferred from site three in Lake St. Clair to the Upper St. Clair River and exposed for 59 days (n =10). Triangles represent the mean body burden of *Elliptio complanata* specimens transferred from Balsam Lake to the purging site.

PURGING of OCS

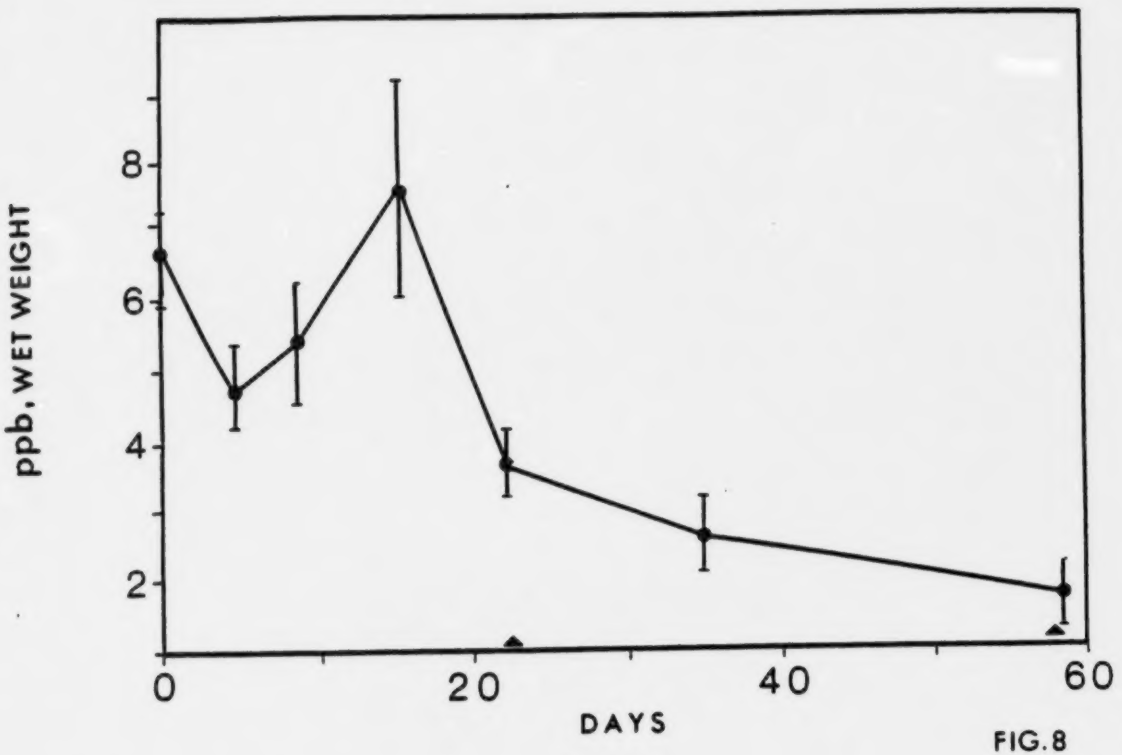

FIG.8

Table 11. Test for differences in the means and a linear purging pattern for the entire purging study of *Lampsilis radiata* mussels in the Upper St. Clair River, using logarithmic values (@=.01).

Contaminant	Differences among means		Linear Regression	
	F-ratio	Sig.	F-ratio	Sig.
HCB	57.57	Yes	7.25	No
OCS	8.67	Yes	2.89	Yes

DISCUSSION

Accumulation of contaminants

Body burdens of QCB, HCB, and OCS did not differ significantly among mussels placed in cages near the surface of the water, one m above the sediment and on the sediment. Thus the vertical distribution of these contaminants in the water column appears to be uniform and the water phase is implied as the primary source of organic compounds for the mussels. Therefore biomonitors deployed near the water's surface will be representative of the microhabitat they are surveying.

After exposure periods up to 81 days the body burdens in the mussels still did not appear to reach equilibrium with the levels of contaminants in the water. This may have resulted from the seasonal effects as discussed later in this section or changes in the source inputs of QCB, HCB, and OCS in the area. Regardless, this observation suggests that exposure times used in some of the previous studies may be too short.

There have been considerable differences observed in the time required for organic contaminants levels in biota to reach equilibrium with concentrations in the water. Kauss et al. (1983) found Elliptio complanata individuals placed in cages in the water column to accumulate detectable levels of PCBs after two to four days of exposure and to equilibrate with the concentrations in the surrounding water within eight days. When exposed to contaminated soil in the laboratory, body burdens of PCBs in Mytilus edulis reached a steady state in twenty days (Pruell et al., 1986). However, Mytilus edulis specimens placed in cages in the North Sea did not reach plateau levels for two to three months (de kock 1983).

Other organism appear to react much more slowly to changes in the ambient contaminant levels. Polychlorinated biphenyl levels did not equilibrate in polychaete worms and shrimp after thirty-two days of exposure (Mcleese et al., 1980). The body burdens of HCB and OCS in oligochaetes exposed to contaminated sediment failed to reach a steady state after 120 days (Oliver 1984). Fathead minnows required 100 days for their levels of PCBs to attain equilibrium (Defoe et al., 1978).

The more erratic pattern observed in the uptake of HCB relative to OCS may indicate that the body burdens of HCB can reflect the ambient concentrations more quickly than OCS. The greater decline in HCB levels observed at Wallaceburg during the last sampling period also suggests a quicker response time for HCB. The chemical properities that may be responsible for these observations are discussed in the depuration section.

Since contaminant levels are similar at Chenal Ecarte and Walpole, a significant portion of the contaminant plume flowing along the Canadian shoreline of the St. Clair River appears to be deflected into Chenal Ecarte. Similar levels found at the Wallaceburg site indicates that the contaminants remain in the channel for a considerable distance. The low levels of QCB, HCB, and OCS observed at Stoney Point and Belle River suggests that these sites are located south of the contaminant plume in Lake St. Clair. This confirms previous findings which indicate that the contaminant patterns near the south shore of Lake St. Clair are not influenced by the organic compounds flowing from the St. Clair River (Muncaster, 1987, Pugsley et al., 1985).

Mussels which were deployed later in the season had consistently greater body burdens than specimens exposed for similar time periods but earlier in the year. This may explain why the body burdens of the mussels did not appear to reach equilibrium with the contaminant concentrations in the surrounding water even after exposure periods of 81 days. The greater body burdens observed in the fall may have resulted from the decrease in water solubility that organic compounds experience with a decline in the water temperature (Dickhut et al., 1986). The lower solubility would correspond to a greater affinity of the contaminants for the lipids in the mussel tissues. Physiological changes in the mussels resulting in alterations of the lipid content or changes in the feeding behaviour may also account for the seasonal variation observed. De kock (1983) found consistently greater PCB burdens in Mytilus edulis individuals placed in the North Sea in the winter relative to those in mussels at similar locations in the summer. The period required for levels of PCBS in the mussels to reach equilibrium with those in the water decreased from 100 to 60 days when mussels were exposed in the winter relative to the summer (de Kock, 1983).

Pattern of Contaminant Loss

Factors that affect the purging rate of a compound are its molecular weight, water solubility, and steric properties, all of which determine its affinity for lipids in the body tissue (expressed by the octanol-water coefficient (K_{ow})) (Geyer *et al.*, 1982). The location and amount of lipids in an organism also influences the behaviour of contaminants.

When transferred to a pristine site in the Upper St. Clair River, the pattern of contaminant loss in *Lampsilis radiata* was chemical specific. The large initial decline of HCB suggested that a portion of the body burden was easily purged when the mussels were placed in a clean environment. Octachlorostyrene displayed no contaminant loss initially. However, over the duration of the study, 58 percent of the OCS burden was lost by the mussels. These results suggest that fluctuations in the HCB and to a lesser degree OCS burdens will reflect short term changes in the contaminant levels in the ambient water.

The chemical properties of HCB and OCS are consistent with the purging observations. Hexachlorobenzene has a lower K_{ow} than OCS and thus should decline more quickly if the ambient contaminant levels are reduced. The lower molecular weight of HCB may permit it to cross membranes more readily and equilibrate with the surrounding medium (Oliver, 1984). Konemann and Leeamen (1980) determined that maximal bioaccumulation occurs in a compound possessing a $\log(K_{ow})$ near 6.5. Spacie and Hamelink (1985) noted that some non-polar organic molecules are able to diffuse rapidly across the lipid bilayer of membranes. This would explain the quick purging of HCB despite its non-polar nature relative to OCS (as indicated by the lower retention time of HCB).

Samples taken on day fifteen of the purging study showed an increase in the body burden of all contaminants. No clear explanation is available for this result, although it is possible that environmental contaminant levels increased during this period. Alternatively, the stress of transportation and handling may have inhibited feeding and resulted in very little purging of some contaminants for the first fifteen days. This has been observed for transplant experiments involving oligochaetes (Oliver, pers. comm.). For OCS, there was no significant difference between the mean body burden at time zero and the third sampling.

The elimination of contaminants is a slower process than the accumulation due to the hydrophobic nature of the toxicants (Boon et al., 1985, Larsson, 1986, Pruell et al., 1986). The ability of L. radiata to eliminate greater than 50 percent of its body burden of HCB within four days represents a very fast purging rate. Although HCB is considered to depurate rapidly from aquatic organisms (Sax, 1984), Tarkpea et al. (1985) calculated a half-life of 81 days for HCB in fish livers. In the same study, Tarkpea et al. (1985) determined a half-life of 143 days for OCS, indicating, as in the present study, the tendency of HCB to be purged more rapidly. PCBs appear to be purged much more slowly, though it is highly dependent on the test organism used (Boon et al., 1985). Defoe et al. (1978) found no appreciable loss in the total body burden of PCBs in fathead minnows after 60 days. There was no obvious excretion of PCBs by polychaete worms during a 26 day exposure (McLeese *et al.*, 1980). The half-life of PCBs in trout was found to be several years (Niimi and Oliver, 1983). A laboratory study by Pruell *et al.* (1986) suggested that mussels may eliminate PCBs more readily. Half-lives of four congeners in *Mytilus edulis* ranged from 16 to 46 days, with slower purging rates associated with the more highly-chlorinated congeners. This contrasts with findings presented here, in which the congener with the greatest chlorination (180) was purged most rapidly. Hornshaw *et al.* (1983) similarly observed that mink eliminated the highly-chlorinated congeners more readily.

Before depuration rates can be estimated, an appropriate kinetic model must be applied to the data. The behaviour of a contaminant within an organism can be represented by either one or two-compartment models, where a compartment is defined as a quantity of pollutant with uniform kinetics of transport and transformation (Connel and Miller, 1984, Spacie and Hamelink, 1985). With the simplest model the entire body burden behaves with uniform kinetics, while two distinct pools, each with their own characteristics, exist in the two-compartment model. Connel and Miller (1984) defined the pool that is more readily lost as the peripheral, or non-assimilated, compartment, this is in equilibrium with the external medium. Uptake and elimination of compounds will occur only via the peripheral compartment. The second pool, which equilibrates with the peripheral body burden, is the central compartment.

When plotted on a logarithmic scale, a one-compartment model produces a negative linear relationship between body burden and time, while an inverse curvilinear correlation between burden and time represents a contaminant exhibiting two compartment characteristics (Spacie and Hamelink, 1986). In the present study, only the loss of OCS showed a significant fit of linear regression after transformation. Hexachlorobezene's depuration rate clearly displayed a non-linear relationship, suggesting the body burden in the mussels was located in two compartments. This may be explained by the lower lipophilicity of HCB, which allowed significant accumulations external to the body tissues. The initial high rate of HCB loss could be attributed to the transfer of the burden from this non-assimilated pool to the water. In contrast, the burdens of OCS and the PCBs appear to have been centralized in a pool, from which the compounds were not easily purged. The behaviour of HCB is inconsistent with the assumption that it represents a one-compartment model in guppies as stated by Konemann and Hansen (1986).

For goldfish, Nagel and Ulrich (1980) identified the gills as the peripheral pool, while the remaining body tissues represented the central compartment. Ninety-five percent of the phenols of low molecular weight and high polarity were eliminated from the gills within four hours, while during the same period ninety-seven percent of the burden in the body was retained. Studies on depuration kinetics of petroleum hydrocarbons and organophosphate insecticides in mussels can also be explained if there are two contaminant compartments (Broman and Ganning, 1986, McLeese *et al.*, 1979).

SUMMARY

The freshwater mussel, E. complanata, illustrated no significant difference in uptake of contaminants throughout the water column or on the sediment surface. This suggests that the water phase might be the main exposure source of the investigated contaminants in the Huron-Erie corridor. Perhaps the most significant observation was the seasonal differences in uptake rates. Comparable exposure periods later in the year resulted in increased body burdens. This might have been a function of either increased loadings to the system or by changes in water temperature affecting the solubility of these compounds in water. Other potential explanations are the reduced absorption of the compounds within the wetland habitats (decreased productivity) or changes in the dissolved organic content of the water mass. Factors regulating seasonality in uptake rates must be resolved before biomonitoring can be applied to critical water quality management concerns.

Site differences were quite evident in uptake patterns. At the Walpole site, where mussels were exposed within the main channel there was a continuous uptake of QCB, HCB, and OCS. The Chenal Ecarte site, however showed a more event type exposure pattern for QCB and HCB, which was even more dramatic at the Wallaceburg site. These observations at the latter two sites demonstrate that other parameters may be regulating contaminant exposures, the influence being more measurable with QCB and HCB as opposed to OCS.

Depuration rates suggest that mussels such as *L. radiata* might be somewhat sensitive to handling. The delay in the depuration of OCS is difficult to explain with regard to sampling or analytical error. Preliminary studies indicate that differences in K_{ow} values may strongly regulate depuration rates and patterns.

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MERCURY IN BENTHIC INVERTEBRATES FROM PENINSULA LAKE AND LAKE VERNON

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M5S 1A4

Introduction

High mercury concentrations in biota have been observed in rivers or lakes that have received mercury discharges from contaminated effluents, such as in the English-Wabigoon River (Rudd et al. 1983) as well as in impoundments lakes or reservoirs (Bodaly et al. 1984; Stokes and Wren 1987). The source of the mercury present in fish in the former case has been attributed to the direct discharge of mercury, while the increase in fish mercury in reservoirs has been related to increased bacterial methylation. This increase in methylation has been attributed to bacterial degradation of flooded vegetation (Bodaly et al. 1984).

However, . fish in lakes that are remote from point source pollution or have not been flooded also have been found to have elevated mercury concentrations. This is the case in several lakes in the Muskoka-Haliburton area where fish mercury levels often exceed the federal guidelines for unrestricted consumption (Suns et al. 1980, 1987; Wren and MacCrimmon 1983). Until now, it has not been clearly understood why fish mercury levels in these lakes can reach levels found in very contaminated ecosystems. Moreover, not only the aquatic ecosystem is at risk but also the terrestrial fauna that rely on aquatic biota as a principal food source. This has been demonstrated by Wren et al. (1986) who found high levels of mercury in wildlife feeding on aquatic organisms in the Muskoka-Haliburton area.

These results suggest that the mercury present in remote lakes can be a threat not only to humans, but also to the wildlife feeding on fish and other contaminated aquatic biota. Yet, very little is known about Hg levels in aquatic organisms other than fish in these lakes. Although fish, especially the the top predators integrate the Hg present in a lake, they can tell us very little about the origin and pathways of Hg.

The overall objective of our study was to to achieve a better understanding of Hg pathways in lakes remote from point sources and impoundments. To acheive this objective, we chose to work on

Table 1. Location and morphometric data on Lake Vernon and Peninsula lake.

	Vernon	Peninsula
Latitude	45o20'	45o25'
Longitude	79o17'	79o07'
Elevation (m)	283	283
Surface (ha)	1443	865
Maximum depth (m)	37	34
Mean depth (m)	12.7	9

benthic invertebrates. We chose these organisms for several reasons. First, benthic invertebrates are an important food source for fish and thus can contribute to the mercury burden in fish. Secondly, the restricted movement of the benthos compared to fish, enables them to be better candidates for the identification of localized sources of mercury if there are any. Finally, we think their role in Hg pathways may be important because of their presence in or in close contact with the sediments which are usually considered as a sink for mercury in heavily contaminated systems.

The specific objective of our study was to evaluate the importance of benthic invertebrates in Hg pathways in lakes remote from point source of mercury. We were especially interested in:

- determining Hg levels in different benthic organisms and evaluating the influence on Hg concentrations of collection site, time of year and organism size.
- comparing Hg levels among benthic invertebrates species or taxonomic groups and estimate the influence of sediment Hg, trophic level or habitat on Hg concentrations observed in the different organisms.

Study area

The study was conducted on Vernon and Peninsula Lakes. Both lakes are located near Huntsville, Ontario. The precise location and morphometric data of the study lakes are shown in Table 1.

The two lakes differ in their Hg concentrations found in fish. Fish mercury levels in Lake Vernon are high; lake trout were found to have up to 10 ug Hg/g in their edible tissues while smallmouth bass had up to 3.6 ug Hg/g (Sherbin 1979). In Peninsula Lake, fish concentrations are lower and do not exceed 1.0 ug Hg/g (Anonymous 1986).

Methods

Field collections and sample preparation

The infauna (invertebrates living in the sediments) was sampled at 7 sites on Lake Vernon (numbered 1 to 7) and one site at its outflow at Hunters Bay (HB) (Figure 1). Six sites were sampled on Peninsula Lake (Figure 2). Ten Ekman grabs (225 cm2) were taken in the littoral zone (0 - 3 m depth) at each site, each month from June through October. Benthic invertebrates were separated from the sediments in a plastic seiving bucket. They were placed in a container with lake water and brought to the lab in a cooler. The most common and largest organisms were (for

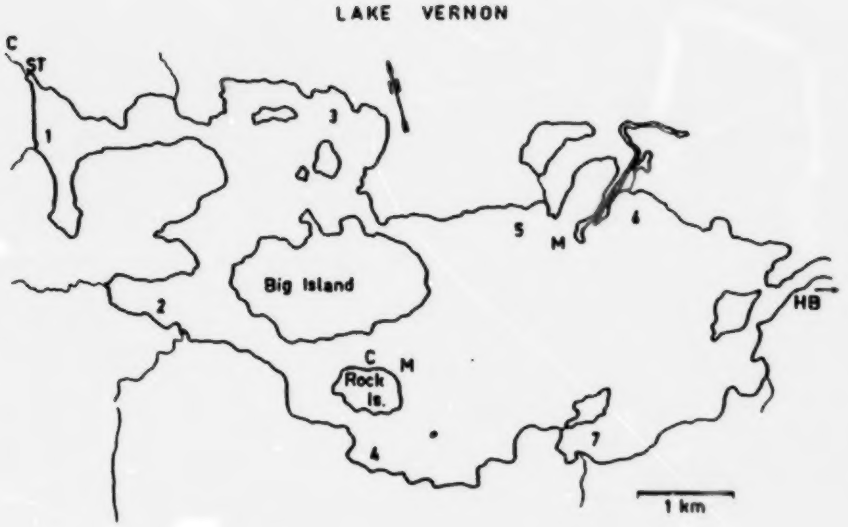
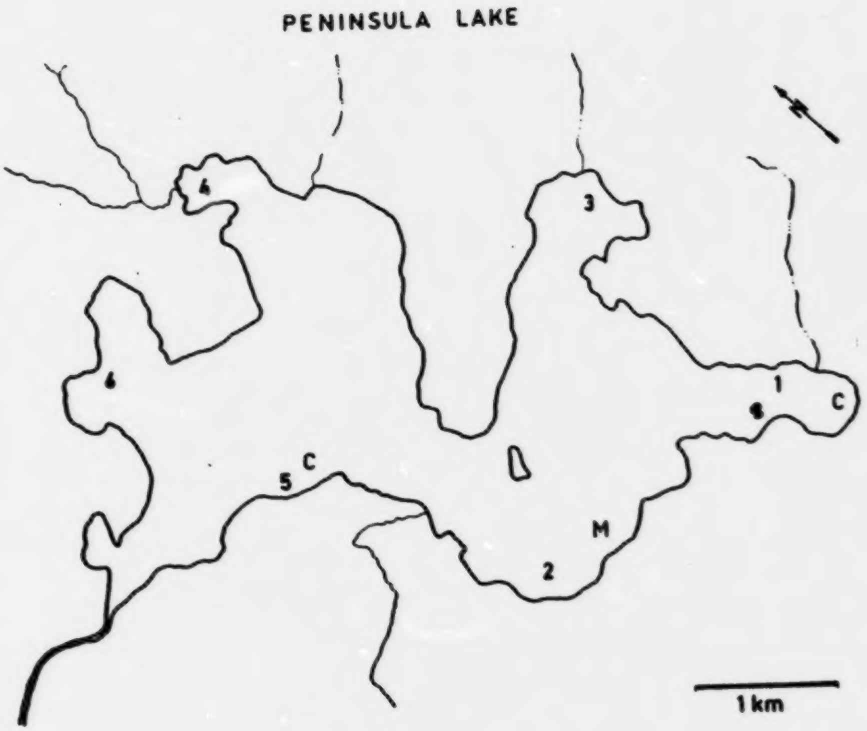

LAKE VERNON
C
ST
1
3
Big Island
2
5
M
6
HB
C
M
Rock Is.
4
7
1 km

Figure 1. Lake Vernon. Sites 1 to 7 and HB were sampled every month from June to October. Freshwater mussels and crayfish were collected at two sites each (indicated by M and C).



PENINSULA LAKE
N
4
3
6
1
C
5
C
M
2
1km

Figure 2. Peninsula Lake. Sites 1 to 6 were sampled every month from June to October. Freshwater mussels were collected at site M and crayfish at sites C.

both lakes) the snail *Campeloma decisum*, the mayfly *Hexagenia* sp., and oligochaetes (Annelida, Oligochaeta). Other organisms, including Odonata, Coleoptera, Trichoptera, and Diptera were also collected and analyzed for Hg, but since they were less common, these results were pooled; we will refer to them as "other" organisms. Additionally, in July and August, invertebrates were qualitatively sampled at Hood Rapids (site ST, Figure 1), one of Lake Vernon's inflows. The total length of all organisms except oligochaetes was measured and organisms were pooled according to their size (often, several organisms were needed to have sufficient biomass for analysis). Then the pooled organisms were dried at 30oC until they reached constant weight. Usually 20 to 70 mg dry weight were used for Hg analysis.

Bivalves, mainly *Elliptio* spp were collected at site 5 and near Rock Island in Lake Vernon (Figure 1) and at site 2 in Peninsula Lake (Figure 2). The collection was done by divers in July and August. However, some bivalves were also found in the grab sampling done at other times. They were included with the remainder of the bivalves. Length, width, and height of each bivalve was measured. After drying, soft tissues of the bivalves were homogenized with a mortar and pestle, and 20 to 60 mg dry weight was used for Hg analysis.

The crayfish *Cambarus bartoni* was also collected in both lakes and in Hood Rapids during July and August. They were collected using minnow traps or by hand when snorkelling. The main collection sites are indicated by (C) in Figures 1 and 2. Cephalothorax length and crayfish total weight were measured for all specimens. Afterwards, the abdominal muscle was removed and Hg analysis was performed on a 180 mg (wet weight) sample.

Surficial sediments were collected in August at each site on Lakes Vernon and Peninsula. Four replicate samples were taken with an Ekman grab, sediments were drained and freezed. Prior to Hg analyses, the sediments were thawed, mixed and 2 to 4 g wet weight were taken for Hg analysis. Water content in sediments was determined on approximately 5 g subsamples dried at 110oC to constant weight. All Hg concentrations were converted to dry weight basis. The percentage of organic matter in sediments was also determined by ashing the dried sediments at 450oC for four hours. Only pooled preliminary results for each lake will be presented here.

Mercury analysis

Invertebrate samples were digested in concentrated sulfuric-nitric acid (4:1) at 230oC in an aluminum hot block for 12-16 hours. Samples were analyzed for total mercury by cold vapor atomic absorption spectrophotometry using a Pharmacia mercury monitor (OMOE, 1983).

Sediment samples were analyzed using the method described by the Ontario Ministry of the Environment (1983).

On each Hg run, every tenth sample was analyzed in triplicate. Of these triplicate samples, one was spiked with 20 ng of inorganic Hg. During each run, standard reference material (oyster tissues, National Bureau of Standards, no 1566) was analyzed in duplicate along with duplicate subsamples of a large homogenized fish. The accuracy of Hg determination in oyster tissues (0.057 ug Hg/g) was estimated to be 1.7% with a precision of 13.8%. Precision on replicate fish Hg (mean of 0.77 ug Hg/g) determinations was 6%. Limits of detection was 0.007 ug Hg/g dry weight for sediments, 0.006 g Hg/g wet weight for crayfish abdominal muscle, and 0.018 ug Hg/g dry weight for smaller invertebrates and bivalves.

Data analysis

We used two-way ANOVA's to test for the influence of site and collection time on Hg concentrations in *Campeloma decisum*, *Hexagenia* and Oligochaeta.

Hg concentrations or body burden were fitted against body size (weight or length) with simple linear regressions. Whenever possible regressions lines were compared with analysis of covariance.

Results and discussion

The influence of site (or lake) or sampling time on benthic Hg concentrations

The effect of site and time of year was tested simultaneously in snails, mayflies and oligochaetes.

In the snail *Campeloma decisum*, mean Hg concentrations in the 115 samples from all sites and sampling times ranged from 0.32 to 2.79 ug/g dry weight (Figure 3). Values for both lakes are consistently higher than the value of 0.10 ug Hg/g wet weight reported by Huckabee at al. (1979) for invertebrates from non-contaminated systems.

Collection site had a significant effect ($p < 0.001$) on Hg concentrations of snails, a result due to very high values at Lake Vernon's outflow (site HB, pooled mean + 1 SD (n): 2.24 + 0.87 (10)). Excluding this site, the mean pooled values at site ST (0.63) and other Vernon sites (0.75) were similar to those at Peninsula sites (0.65).

Sampling time also had a significant effect ($p < 0.001$) on Hg concentrations. Snails collected in June, July, August had higher Hg concentrations (0.891, 1.035, 0.979 respectively) than snails collected in September and October (0.620 and 0.509).

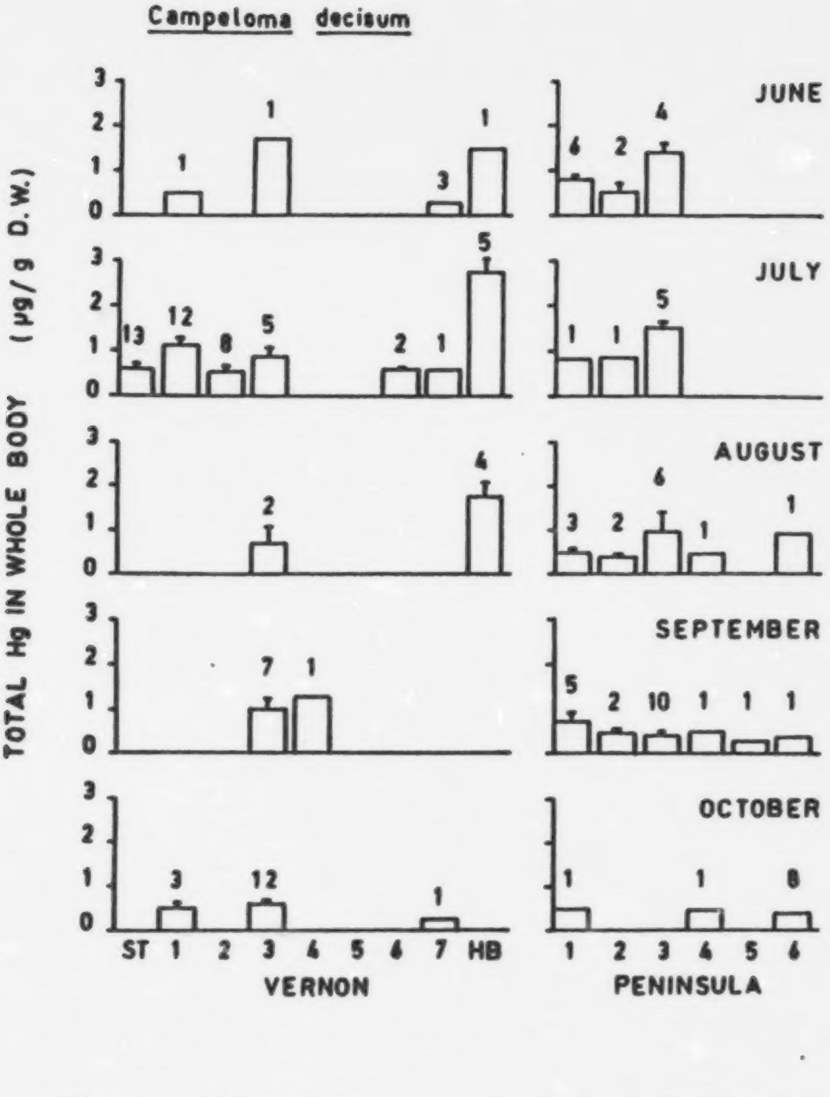


Figure 3. Hg concentrations (Mean + 1 Se, n) in the snail *Campeloma decisum* at different sites and time.

The interaction of site and month was as well significant ($p < 0.01$). At any given site where we have sufficient data, mean Hg concentrations at the beginning of the season tended to be higher than at the end. However the significance of time and site on concentrations should be interpreted cautiously given the high coefficient of variation (42 to 128 %) often observed in Hg concentrations in samples collected at the same time and site.

Mean Hg concentrations in the mayfly Hexagenia ranged from 0.01 to 0.28 ug/g, an order of magnitude lower than that for snails (Figure 4). Since analyses were performed on only 58 samples from different combinations of site/month, samples from sites within each lake were pooled for data analysis. We found no difference in Hg concentrations between the two lakes and no differences among months. We also found no significant interaction between lake and month on Hg concentrations.

Mean Hg concentrations in oligochaetes fell within the same range as that for mayflies, ranging from 0.04 to 0.27 ug/g (Figure 5). As for mayflies, due to the small sample size (44) data within one lake were pooled for each month. Again, there was no significant effect due to lake or month, and no lake/month interaction effect on Hg concentrations in oligochaetes.

Differences in Hg concentrations between snails, mayflies, and oligochaetes might be explained by differences in habitat and/or diet. All three groups are usually found buried in the sediments, however the snail Campeloma decisum has been seen foraging at the sediment-water interface or on wood logs. Both oligochaetes and mayflies ingest sediments to obtain their food, while the snails are more herbivorous, thus explaining their presense at the surface of sediments. However this explanation does not account for the large variation in Hg concentrations that occured within each group collected at the same site and at the same time. This variation may be attributable to organism size.

Influence of organism size on Hg concentrations

We found an inverse relationship between Hg concentrations and body weight for snails (Table 2). The largest snails (100 mg) had Hg concentrations that were in the same order of magnitude as the highest concentrations observed in mayflies or oligochaete (0.30 ug Hg/g), while smaller snails (< 20 mg) had concentrations often higher than 1 ug Hg/g. For mayflies, no significant relationship was found between body weight and Hg concentrations (Table 2), although an inverse trend was also observed.

For the bivalve Elliptio complanata, there was a positive correlation between size and Hg concentrations in Lake Vernon,

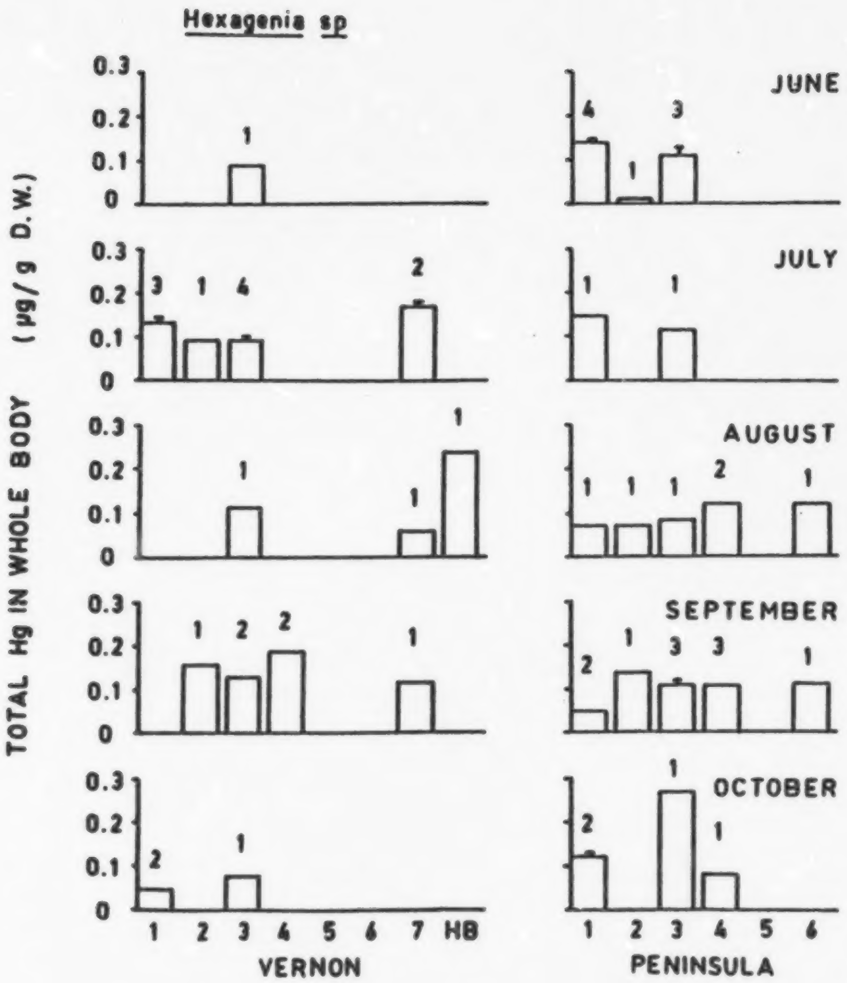


Figure 4. Hg concentrations (Mean + 1 SE, n) in the mayfly *Hexagenia* sp at different sites and time.

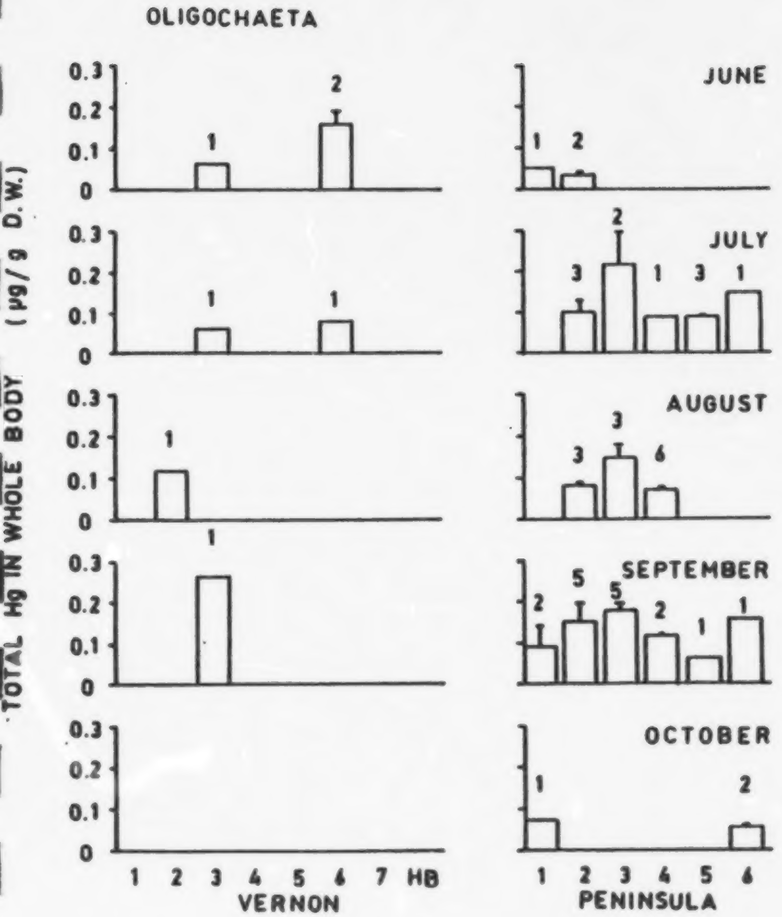


Figure 5. Hg concentrations (mean + 1 SE, n) in oligochaetes (Annelida, Oligochaeta) at different sites and time

Table 2. Relationship between Hg concentrations and organism weight in *Campeloma decisum* and *Hexagenia* sp. $* p < 0.05$, $*** p < 0.001$.

Organism	Lake	Site	Month	n	r
C. decisum	Vernon	1	08	12	- 0.386
		2	07	8	- 0.908 ***
		ST	07	13	- 0.631 *
	Peninsula	1	08	9	- 0.721 *
Hexagenia sp.	Vernon	pooled		28	- 0.217
	Peninsula	pooled		30	- 0.261

while no such correlation was observed in Peninsula Lake (figure 6). However, in Peninsula, only small mussels under 65 mm length were found. Mussels of similar size in Lake Vernon also did not show a size-Hg relationship. Nevertheless, mussels from Lake Vernon that were under 65mm length had significantly higher ($p < 0.001$) Hg concentrations (mean of 0.432 ug Hg/g) than those from Peninsula (mean of 0.201 ug/g).

For the crayfish, *Cambarus bartoni*, we have observed a significant positive relationship between total weight and Hg concentrations in abdominal muscle (Figure 7). Similar to the mussels analyzed, Hg levels in crayfish from Lake Vernon were significantly higher than those from Peninsula lake.

The positive relationship between size and Hg concentration found in bivalves and crayfish are similar to those often observed for fish species (Scott 1974, Mathers and Johansen 1985). The negative correlation observed in snails might be due to surface adsorption since the surface/volume ratio is often higher in smaller organisms or alternatively to biodilution of the Hg at larger size.

Differences in Hg between lake and stream organisms

Crayfish collected in Hood Rapids (site ST), one of Vernon's inlets, had significantly higher mercury levels than crayfish collected in Vernon lake (Figure 7).

We also compared the body burden-size relationship of stream invertebrates (Lake Vernon only) to those of lake invertebrates (snails, mayflies, oligochaetes excluded). Organisms collected from the stream were different from those found in the lakes. However, for the purpose of the comparison most of the organisms included were predators (Table 3). Organisms collected from the stream were collected on rocks, while the majority of lake organisms were collected from the sediments with the exception of the Coleoptera from Vernon lake that were collected at the water surface (Table 3).

The slope for Vernon stream organisms was significantly higher than the slope for Peninsula or Vernon lakes, while there was no difference between Peninsula Lake and Lake Vernon (Table 4).

Comparisons of Hg concentrations in benthic invertebrates and sediments

The preliminary results of mercury concentrations and organic matter content of sediments suggest that there was no significant differences in these variables between the two lakes (Table 5).

Mean Hg concentrations in the smaller fauna living in the

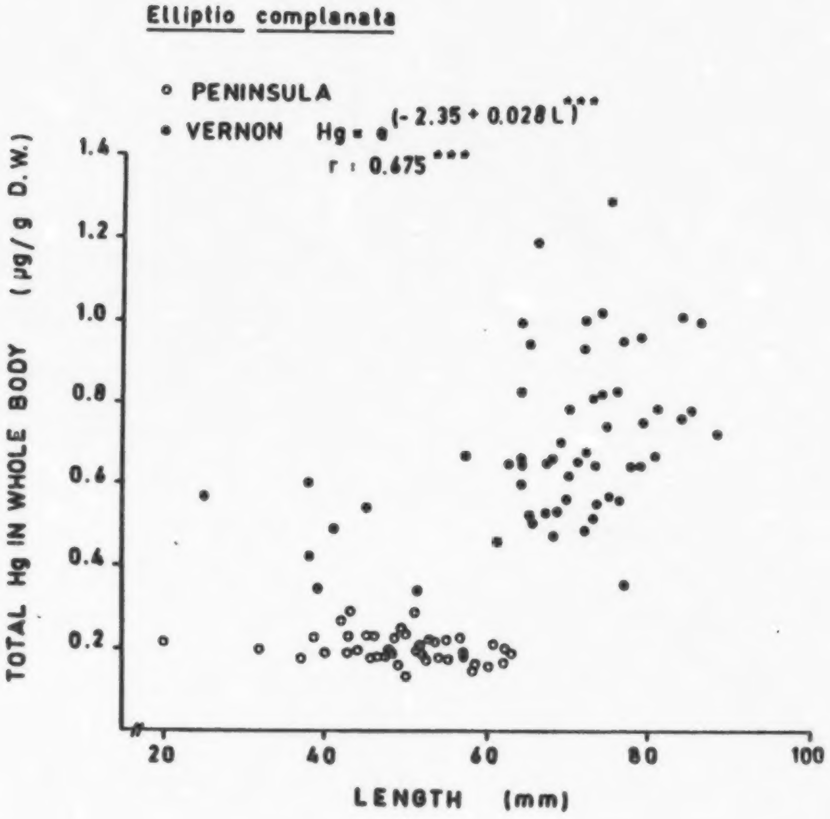


Figure 6. Relationship between Hg concentrations and length in the mussel *Elliptio complanata* from Lake Vernon and Peninsula Lake.

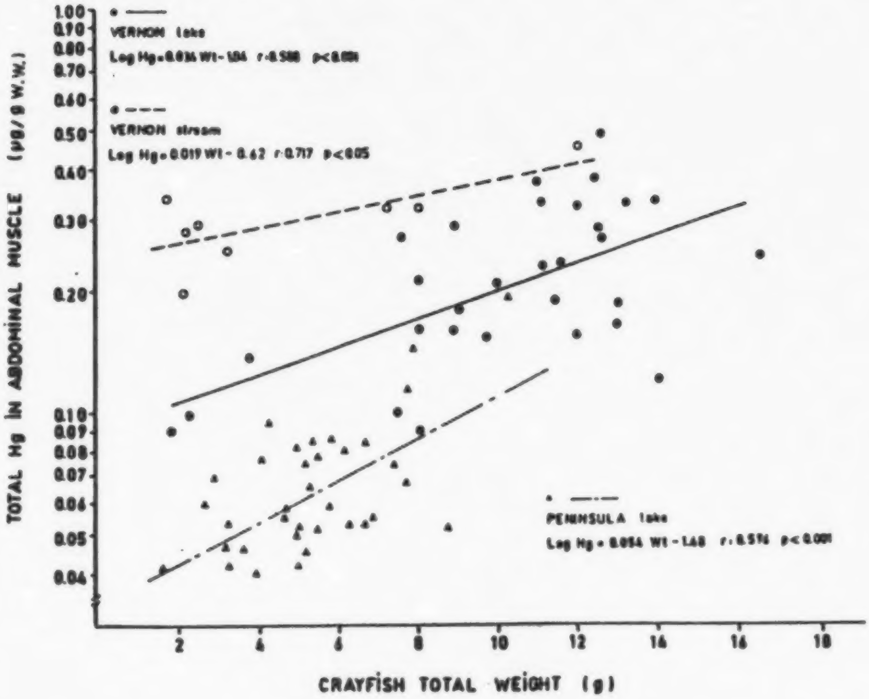


Figure 7. Hg concentrations against total weight in the crayfish Cambarus bartoni from Lake Vernon (lake), Lake Vernon (stream) and Peninsula Lake (lake).

Table 3. List of organisms included in the body burden - size comparisons for Lake Vernon, Vernon stream and Peninsula Lake.

Site	Organism		Trophic level	Habitat	n
Vernon Lake	Odonata	*Dromogomphus*	P	Sed.	10
		other	P	Sed.	3
	Coleoptera	*Dineutus*	P	Wat.	6
		Gyrinus	P	Wat.	11
	Other	misc.	P	Sed.	1
		misc.	D	Sed.	6
Vernon stream	Odonata	*Gomphus*	P	Rocks	7
		other	P	Rocks	1
	Trichoptera	*Nyctiophylax*	P	Rocks	11
		Ceratopsyche	F	Rocks	5
		other	D	Rocks	1
	Plecoptera	*Acroneuria*	P	Rocks	5
	Diptera	*Holorusia*	D	Sed.	2
Peninsula Lake	Odonata	*Dromogomphus*	P	Sed.	8
		Gomphus	P	Sed.	3
		other	P	Sed.	4
	Gasteropoda	misc.	D	Sed.	10
	Other	misc.	P	Sed.	2
		misc.	D	Sed.	14

P: predator, D: deposit feeder, F: Filter feeder, Sed.: sediment Wat.: water.

Table 4. Relationship between Hg body burden (ug) and weight (g) of organisms listed in table 3 (body burden and weight transformed to their log values). *** $p<0.001$.

Site	Slope	Intercept	n	r
Vernon stream	1.40	0.093	32	0.881 ***
Vernon lake	0.95	-1.04	37	0.966 ***
Peninsula lake	0.94	-1.16	41	0.920 ***

sediments (with the exception of snail), were usually lower than concentrations observed for larger organisms. Hg in the infauna was not significantly different between both lakes. These levels probably reflect the Hg levels present in the surrounding sediment. In contrast, higher Hg concentrations in snails versus oligochaetes, mayflies or others may reflect differences in foraging habits.

Benthic Hg concentrations between the two lakes were significantly different only for organisms living at the sediment/water interface such as bivalves and crayfish. Differences in water or food Hg levels between the two lakes might account for this difference. In term of food, *Elliptio complanata* is a filter-feeder while the crayfish is omnivore, usually scavenging in or at the surface of the sediments. However, since there is no difference in sediment fauna Hg and sediment Hg between the two lakes, it is unlikely that food could account for the difference. This leaves differences in water Hg to account for the difference in Hg levels in bivalves and crayfish between the two lakes. Regarding the difference found between lake and stream organisms, the highest Hg levels that were observed in Vernon stream might indicate an area where Hg concentrations are higher or where it is more available for uptake by organisms.

Conclusion

Crayfish were found to have the highest Hg concentrations of all organism sampled. Since they can constitute a major food source for fish, especially smallmouth bass, they may account for one of the major sources of Hg for some fish.

Sediment Hg can not account for higher Hg concentrations in mussels and crayfish from Lake Vernon than in Peninsula Lake. It is likely that water Hg may be important in determining Hg levels in these organisms. More research is needed on the relative importance of water Hg relative to food Hg as routes of exposure.

Small streams were identified as an area where Hg concentrations might be higher than in lakes, or where it is more bioavailable. Perhaps we should focus more on these small streams to understand why fish mercury could be so high in areas unaffected by point-source pollution.

Acknowledgements

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Table 5. Preliminary results on Hg concentrations and organic matter in sediments.

	Site	n	Mean	SE	(range)
Hg (ug/g d.w.)	Peninsula	6	0.050	0.006	(0.026-0.069)
	Vernon	10	0.062	0.021	(0.007-0.218)
Organic matter (%)	Peninsula	6	5.9	1.1	(1.2 - 13.4)
	Vernon	10	2.8	2.1	(0.8 - 12.2)

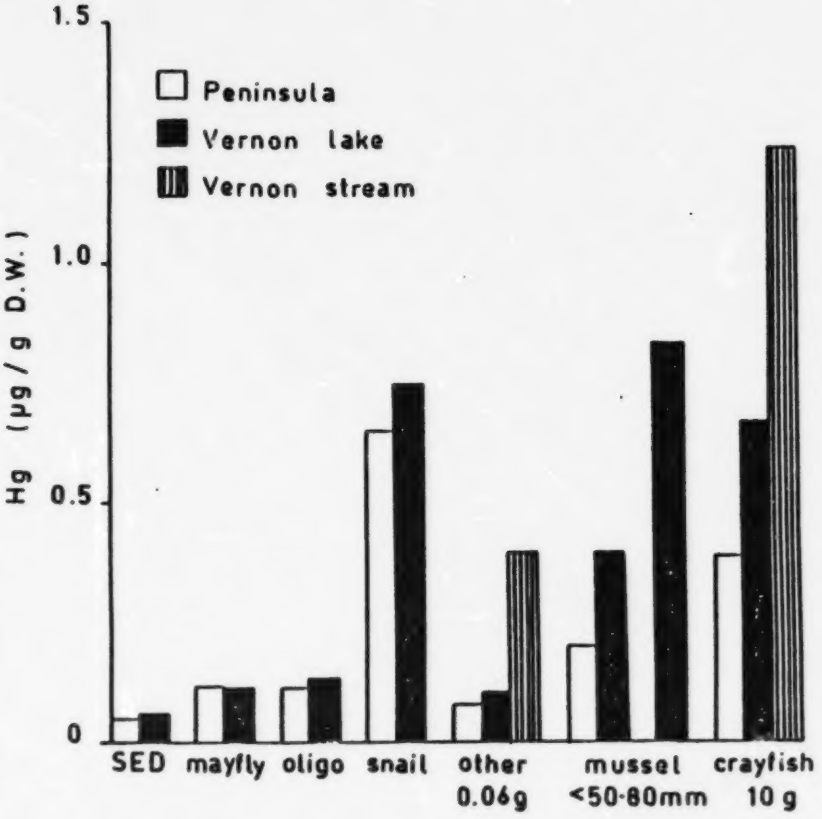

Figure 8. Comparisons among mean Hg concentrations in the different benthic invertebrates and sediments (SED).

invertebrates and Peter Cop did the mercury analysis, their help is greatly acknowledged. Martine Allard had a NSERC postdoctoral fellowship.

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TEMPORAL AND SPATIAL VARIATIONS IN METAL CONCENTRATIONS OF ZOOPLANKTON IN CENTRAL ONTARIO LAKES.

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INTRODUCTION

The concentration of many trace metals is currently elevated in the atmosphere and in precipitation, principally because of the smelting of metallic ores and the combustion of fossil fuels (Jeffries & Snyder 1981; Galloway et al 1982). Trajectory analyses of air parcels indicate these metals may travel hundreds of kilometers in the atmosphere prior to deposition (Thrane 1978). Examination of metal profiles in sediments of remote lakes (Galloway & Likens 1979), in cores of remote bogs, in undisturbed soils of high elevation forests (Friedland et al 1984) and in cores of glacial ice (Jaworowski et al 1975) all indicate that the deposition rates of such metals as Ag, Au, Cd, Cu, Hg, Pb, Sb, Vd, and Zn in remote locations has increased significantly in a few decades.

Despite many years of study on the bioavailability and bioaccumulation of these metals (Phillips & Russo 1978; Coombs 1980; Forstner & Whittmann 1983; Luoma 1983; and others), models for predicting metal levels in aquatic biota are not generally available. This is of concern as several metals (e.g. As, Cd, Cu, Pb, Ag, Hg) are known to accumulate in aquatic biota. Since many metals are inherently toxic they may threaten the health of consumers of the biota, including fish, mammals, birds and man.

Zooplankton were chosen for the study of metal bioaccumulation because: The crustacean zooplankters are known to accumulate high levels of a variety of metals; they are relatively homogeneously distributed in lakes and may be found at any time in virtually all lakes; they have much higher metal levels than their ambient water; they have short gut passage times permitting the collection of large samples that are relatively free of both internal and external metal contamination.

The literature (cited above) indicates that the bioaccumulation of metals may be influenced by lakewater pH, and the concentrations of dissolved organic carbon and Ca, three variables whose levels range widely in Ontario lakes. Even in the absence of local sources, we might therefore anticipate large variations in metal burdens in the zooplankton of Ontario lakes. As large quantities of metals have been discharged into the atmosphere from Sudbury-based smelters, an even larger range might be anticipated.

The overall objective of the present research is to determine if the planktonic concentrations of a variety of trace metals may be predicted from (a) the proximity to a known large point source of metal emissions, (b) the pH, Ca, or dissolved organic carbon levels of the lakewaters, (c) the Ca content of the plankton (Wright 1980), and (d) the composition of the planktonic communities. In this report the within-lake variability of metal levels in zooplankton is described in relation to objectives (b), (c) and (d). Patterns among lakes cannot be evaluated until patterns within lakes are understood. A preliminary assessment of objective (a) is also presented.

MATERIALS AND METHODS

On a single occasion, replicate samples were collected for water and zooplankton from 38 lakes located along a transect running southeast from Sudbury, Ontario for approximately 300 km. The lakes were chosen to range widely in pH, Ca content and dissolved organic carbon content (Table 1), and in distance from Sudbury (Fig. 1).

Working from a fibreglass boat, water samples were collected from near mid-lake at the mid-point of the epilimnion using a peristaltic pump. Water samples were returned to the Ontario Ministry of Environment laboratories at either Dorset or Toronto, Ontario and analysed for pH, Ca, Mg, TP (total phosphorous), DOC (dissolved organic carbon), colour, Fe, Mn, conductivity and alkalinity. Sample collection, preservation and analytical techniques followed Locke and Scott (1986) and OME (1984).

Net plankton samples were collected for metal analyses with a conical tow net (0.75 m dia., mesh size 250 u) from a depth of 3X Secchi depth or 2 m from the bottom, whichever was the shallower depth. All metal parts of the plankton net, including the stainless steel ring, were coated with silicone. The net plankton samples were stored in acid-washed plastic bottles and frozen upon return to the laboratory. All samples were simultaneously subsequently thawed, transferred under filtered laminar air flow into new, acid washed, plastic scintillation vials, dried at 60 +/-2 C, and transferred to the Inorganic Trace Laboratory of the Ontario Ministry of Environment in Toronto for metals analyses. There each sample was redried to constant weight, weighed and transferred in its entirety into a 50 ml glass tube. Six ml of concentrated HNO3 was added and each sample was digested for 2 hr, first at room temperature, then at 50 C. Sample solutions were then heated to 150 C and allowed to evaporate to dryness. An additional 10 ml of acid was added and the evaporation step was repeated. Finally, 5.2 ml of 3.9% HNO3 was added to the tubes which were then heated to 150 C for 30 min, removed from the hot block, cooled and made up to 25 ml with double-distilled water.

Sampling began on May 28 and ended on September 25, 1985. Because nearly four months had elapsed between the beginning and the end of the survey, a study was done to determine whether concentrations of metals in zooplankton varied over time within a single lake. Coeffiecients of variation of metal levels in zooplankton in the 38-lake survey were compared to coefficients of variation in data derived from collections made over a two-year period from Plastic Lake, a nutrient-poor shield lake that has been the focus of intensive studies by staff of the MOE (Ontario Ministry of Environment) (Dillon et al 1987). All samples were collected at the deepest station in Plastic Lake. Water and net plankton samples were routinely collected on a biweekly basis in 1985 and 1986 and subsequently analyzed as described above for the 38-lake survey.

In order to estimate the magnitude of the spatial heterogeneity in the metals composition of net plankton, metal determinations were also performed on net plankton collected on September 24, 1986 at 8 randomly positioned stations in the main basin of Red Chalk Lake, another MOE study lake. The samples were treated as described above for the 38-lake survey.

The zooplankton samples were analyzed for levels of Co, Cr, Ni, and Pb using ICP (Inductively Coupled Plasma) Mass Spectroscopy, and for levels of Ca, Mg, Sr, Fe, Mn, Ti, Sc, Ba, Be, Cd, Cu, Zn, B and Al using ICP Atomic Emission Spectroscopy. Accuracy and precision checks were made with NBS oyster tissue and sample:blank ratios for Zn, Cd, Be, Fe, B, Mn, Mg, Al, Ca, Cu, Ti, Sr, Ba, Pb (Fig. 2). We discarded Ni, Cr, and Pb data from Plastic Lake because precision was poor, Co and Sc because they were rarely detected and Cu, Be and B because the sample:blank ratios approached unity; average ratios of > 10:1 were considered acceptable. Sr data were precise but exhibited low values. We could not verify the accuracy of Al, Ba and Ti analyses because certified values were not available, but they were retained because sample:blank ratios were acceptable, precision was good and patterns in the data were clear and interpretable. Therefore, for the Plastic Lake data analyses were confined to Ca, Mn, Sr, Ba, Ti, Fe, Al, Mg, Zn and Cd. We retained Cu and Ni data for the survey lakes as the range in observed values was so large that differences among lakes seemed to be accurately relected in the analyses.

Zooplankton composition in the survey lakes was determined from additional samples collected in single vertical hauls with the 250 u mesh tow net and in Plastic Lake with the flow meter portion and attached 76 u mesh net in addition to the 250 u mesh net. All samples were preserved in the field with chilled, sucrose formalin.

Edmondson (1959) was the principle taxonomic reference used during sample counting, with Korinek (1981), Deevey & Deevey (1971) and Dodson's (1981) revision of Brooks (1957) consulted for Diaphanosoma, Eubosmina, and Daphnia, respectively. When necessary, subsamples were taken with a Folsom plankton splitter. The tow samples were enumerated to determine the proportional contribution of taxa to the net plankton (> 250 u) standing crop. Zooplankton biomass was estimated by measuring an average of 300 specimens for each crustacean species with a semi-automated electronic calipers, identical to those described by Sprules et al (1981), and then applying the derived length-frequency data to length-weight relationships of Yan and Mackie (1987) and Sprules (pers. comm.).

Data from three lakes which had extremely high Ti levels in the zooplankton were discarded on the assumption that samples were contaminated with bottom sediments. To determine the effect of distance from Sudbury on metal levels in zooplankton, data were first log transformed to improve normality, then six lakes near Sudbury (including the Kilarney area) were separated out of the data set and the mean and 95% confidence interval of the log of the metal levels in the zooplankton were compared between the two data sets (Sudbury lakes and non-Sudbury lakes).

RESULTS AND DISCUSSION

Levels of Cd, Zn, Fe, Mg, Al, and Be were not significantly different between Sudbury area lakes and non-Sudbury area lakes (Fig. 3). Levels of Ti, Ca, Sr, Ba and Mn are lower while levels of Ni and Cu are higher in

Sudbury area lakes than in more remote lakes (Fig. 3). The high levels of Ni and Cu are not surprizing. Indeed, even higher values might be anticipated in the several acid lakes in the Sudbury set.

Fig. 4 compares the coefficient of variation of metal levels in zooplankton among the lake survey data, the two years of data from Plastic lake and the eight-station survey of Red Chalk Lake. The concentrations vary by more than six orders of magnitude. The coefficient of variation in Plastic Lake, especially 1986, often approaches (e.g. Fe, Mn, Mg, Ca) or even exceeds (e.g. Sr, Ba) that of the survey.

It is interesting to note that many of the metals with the greatest temporal variation are essential elements (e.g. Ca, Mn, Fe, Mg). Perhaps biological mechanisms (changes in growth-mediated uptake rates of metals by zooplankton species) may have as much or even greater influence on controlling levels of metals than the physical and chemical mechanisms that control their spatial variation among low alkalinity lakes. All metals have relatively low coefficients of variation among the eight sites in the circumneutral lake, Red Chalk Lake, Ti being an exception.

Groups of metals displayed four types of temporal patterns in Plastic Lake. (1) Levels of Mn, Ca, Sr and Ba increased to maximum levels in the late fall of 1985, but to even higher levels in the summer of 1986 (Fig. 5). The pattern with Fe and Al was similar but peak levels occurred in the fall of 1985 (Fig. 6 (2) Ti behaved similar to Fe and Al in 1986, but in 1985 peak levels were observed in both early spring and late fall (Fig. 6). (3) Mg and Zn levels tended to show less seasonal (i.e spring vs summer or fall) variation than other metals (Fig. 7); (4) Cd had a somewhat unique seasonal pattern with a maximum "pulse" in the late spring in both years (Fig. 8). Spearman Rank correlations on the two years of Plastic Lake data show that the levels of many metals are highly correlated (Table 2).

The patterns of seasonal variations of Mn, Ca, Sr and Ba in Plastic Lake are remarkably similar, yet the differences between the two years are more remarkable. The only metal that behaved similarly in each year was Cd, with Mg, Zn, Ti, Fe and Al showing progressively greater disparity in patterns between years. Some of the differences between or within years may certainly be attributable to changes in water chemistry; pH, Fe and Al, for example, show great seasonal variation in metalimnetic waters (Figs. 9c,e), while other elements, such as Mg, Mn and Ca (Figs. 9b,d,g), show little or no seasonal variation.

The low zooplankton metal levels in the spring may be related to low pH (Fig. 9a), or to the relative absence of Cladocera. The high Al, Fe and Mn levels in the fall of 1985 may be related to the collection of relatively small amounts of filamentous desmids in the net plankton samples. At that time these green algae formed up to about 5% of the net plankton biomass. Desmids are known to accumulate very large amounts of Fe and Mn (Round 1973; Lorch 1978). Since Al levels average 10^4 ug/g in filamentous greens in Plastic Lake (Bailey and Stokes 1985), up to 800 of the approximately 900 ug/g of Al found in the fall of 1985 may be attributable to the algae in the samples.

Seasonal changes in the relative contribution to the biomasses of *Holopedium gibberum*, *Daphnia pulex*, *Diaptomus minutus*, Cyclopoida (mainly *Cyclops scutifer* and *Mesocyclops edax*) and other Crustacea are shown in Fig. 10. The average biomass was similar in each year, but there were large within and between year changes in composition. *Holopedium gibberum*, a weakly calcified cladoceran, was the dominant cladoceran in 1985, but *D. pulex* replaced it as the dominant cladoceran in September of 1985 and in the summer of 1986. Cyclopoida were the largest proportional contributors to toatl biomass in the spring of 1985 and in the spring and fall of 1986. Filamentous green algae, mainly the acidophilic desmid, Goenbladia neglecta, were detected in samples only in the fall of 1985 when they formed 1.2, 2.4 4.2 and 2.0% of net plankton on September 22, October 8, 22 and November 6, respectively. Spearman Rank correlations (Table 3) indicate strong metal-community composition patterns in Plastic Lake, especially for Ca (Figs. 11, 12), Cd (Fig. 13) and Al (Fig. 14).

The net plankton metal data are highly structured and are currently being analyzed by NMDS (non-metric multidimensional scaling). It is anticipated that NMDS will be especially helpful for explaining seasonal changes in the zooplankton species composition.

ACKNOWLEDGEMENTS

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TABLE 1. Ranges and mean values of some water quality variables of lakes studied in the 38-lake survey.

Variable	Mean	Range
Alkalinity, TIP (mg/L)	12.75	-1.2 to 114.2
pH	6.50	4.68 - 8.32
Calcium (mg/L)	6.24	0.57 - 34.7
Conductivity (µmhos/cm)	59	19 - 203
Manganese (µg/L)	41.9	2 - 230
Iron (µg/L)	173	4 - 930
Dissolved Organic Carbon (mg/L)	5.19	0.1 - 32

TABLE 2. Spearman Rank correlations between zooplankton metal levels in 1985 and 1986 Plastic Lake samples. Spearman's r is significant at $P < 0.01$ when $r > 0.45$ ($n = 27$).

Correlation	Zooplankton levels of									
Matrix	Zn	Cd	Fe	Mn	Mg	Al	Ca	Ti	Sr	Ba
Zn-Zoopl	1.00	0.52	0.63	0.25	0.79	0.64	0.39	0.65	0.41	0.44
Cd-Zoopl		1.00	0.67	0.30	0.47	0.56	0.43	0.74	0.45	0.44
Fe-Zoopl			1.00	0.44	0.44	0.70	0.44	0.30	0.48	0.48
Mn-Zoopl				1.00	-0.04	0.50	0.84	0.26	0.88	0.85
Mg-Zoopl					1.00	0.43	0.16	0.57	0.16	0.22
Al-Zoopl						1.00	0.64	0.70	0.69	0.68
Ca-Zoopl							1.00	0.36	0.99	0.97
Ti-Zoopl								1.00	0.41	0.40
Sr-Zoopl									1.00	0.98
Ba-Zoopl										1.00

TABLE 3. Spearman Rank correlations between % biomass of *Holopedium gibberum* (H. gib), *Daphnia pulex* (D. pul), *Diaptomus minutus* (D. min), Cyclopoida (Cyclo) and other Crustacea (Other) and zooplankton metal levels in 1985 and 1986 Plastic Lake samples. Spearman's r is significant at $P < 0.01$ when $r > 0.45$ ($n = 27$).

Correlation Matrix	% H. gib	% D. pul	% D. min	% Cyclo	% Other
Zn-Zoopl	-0.019	0.072	0.150	-0.297	-0.111
Cd-Zoopl	0.309	0.037	0.161	-0.716	-0.100
Fe-Zoopl	0.302	0.152	0.043	-0.657	-0.233
Mn-Zoopl	-0.224	0.763	0.151	-0.433	0.040
Mg-Zoopl	0.292	-0.268	0.009	-0.236	0.052
Al-Zoopl	0.040	0.236	0.270	-0.677	-0.177
Ca-Zoopl	-0.330	0.762	0.159	-0.590	-0.042
Ti-Zoopl	0.419	-0.005	-0.196	-0.624	-0.189
Sr-Zoopl	-0.263	0.760	0.144	-0.609	-0.039
Ba-Zoopl	-0.243	0.720	0.157	-0.595	-0.042

CAPTIONS TO FIGURES

Fig. 1. Map of study area showing locations of lakes with *Holopedium gibberum* (solid circles) and without (open circles).

Fig. 2. Comparison (mean with 95% confidence interval in parentheses) of certified metal levels in NBS oyster tissue with levels determined by ICP analyses (n = 7) in this study.

Fig. 3. Mean levels of 13 metals (and 95% confidence interval in parentheses) in zooplankton in 6 Sudbury lakes and 29 lakes remote from Sudbury.

Fig. 4. Variation in zooplankton metal data among lakes (compare lake survey bar with other bars), over time (compare Plastic Lake yr1 and yr2 bars with other bars) and space (compare Red Chalk (RC) Lake bar with other bars).

Fig. 5. Variations in mean levels of Mn, Ca, Sr and Ba in zooplankton in Plastic Lake during the ice-free seasons of 1985 and 1986.

Fig. 6. Variations in mean levels of Ti, Fe and Al in zooplankton in Plastic Lake during the ice-free seasons of 1985 and 1986.

Fig. 7. Variations in mean levels of Mg and Zn in zooplankton in Plastic Lake during the ice-free seasons of 1985 and 1986.

Fig. 8. Variation in the mean level of Cd in zooplankton in Plastic Lake during the ice-free seasons of 1985 and 1986.

Fig. 9. Variations in (A) pH, (B) Mn content, (C) Fe content, (D) Mg content, (E) alkalinity-TIP, (F) total Al content, (G) Ca content and (H) Dissolved organic carbon content in Plastic Lake during the ice-free seasons of 1985 and 1986.

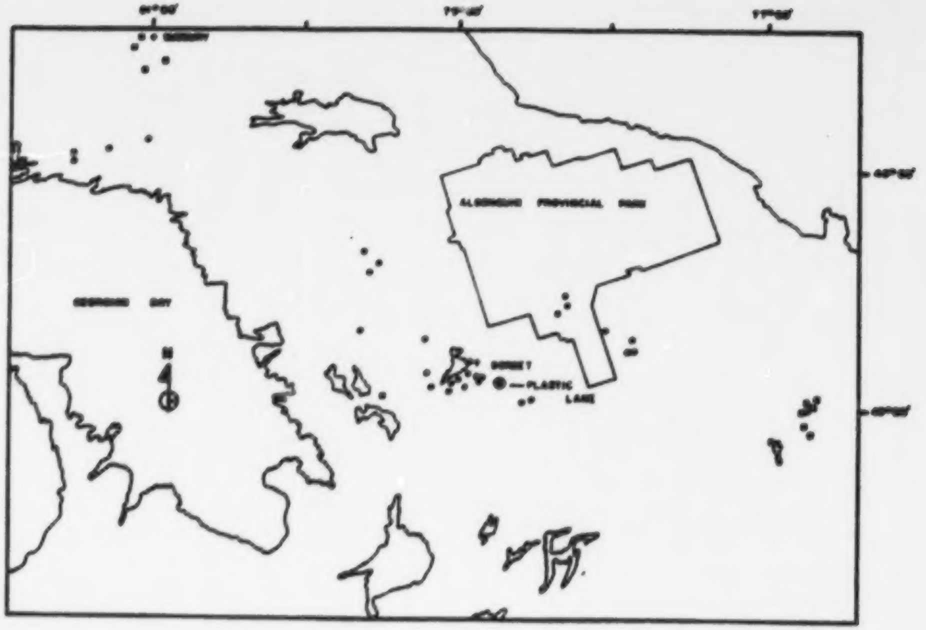
Fig. 10. Variations in biomass of *Holopedium gibberum*, *Daphnia pulex*, *Diaptomus minutus*, filamentous green algae, Cyclopoida, and other Crustacea in Plastic Lake during the ice-free seasons of 1985 and 1986.

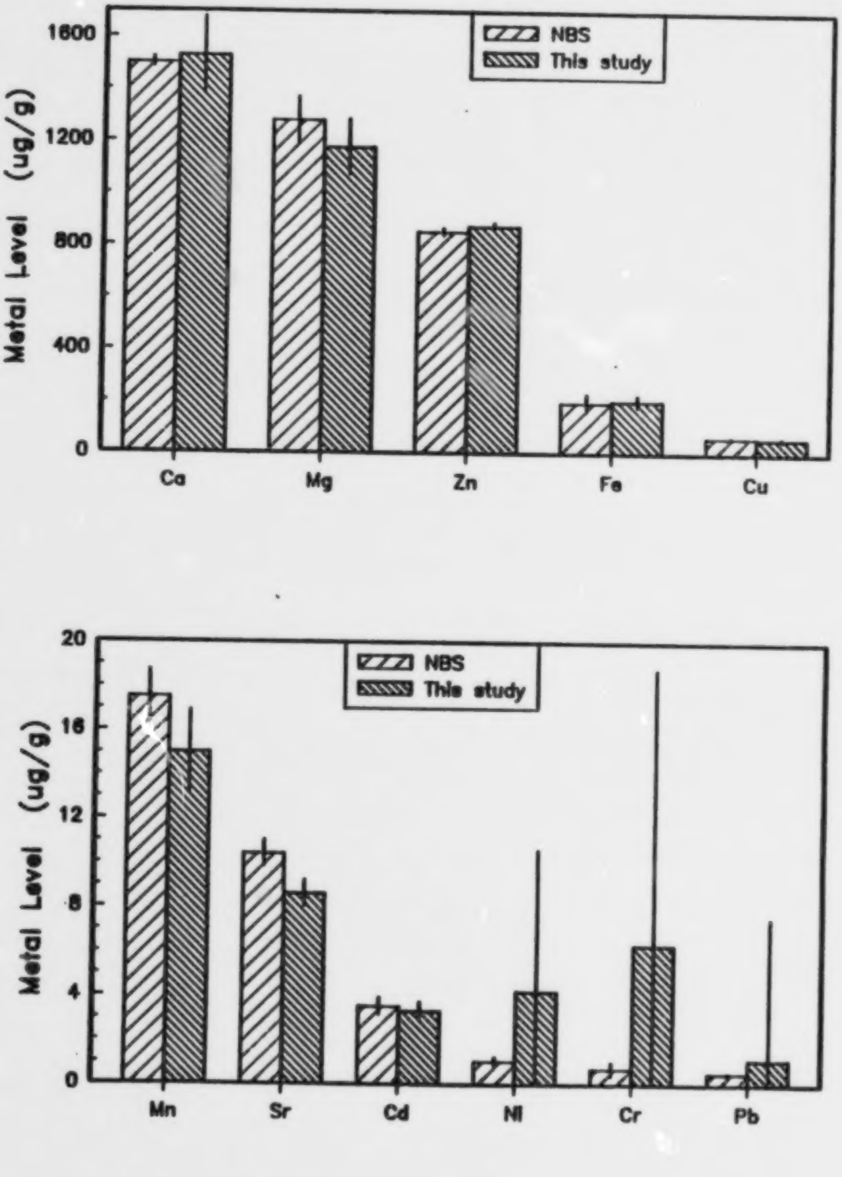
Fig. 11. Relationship between Ca levels (log transformed) in zooplankton and the biomass of *Daphnia pulex* (as proportion of total biomass) in Plastic Lake (based on 1985 and 1986 data).

Fig. 12. Relationship between Ca levels (log transformed) in zooplankton and the biomass of Cyclopoida (as proportion of total biomass) in Plastic Lake (based on 1985 and 1986 data).

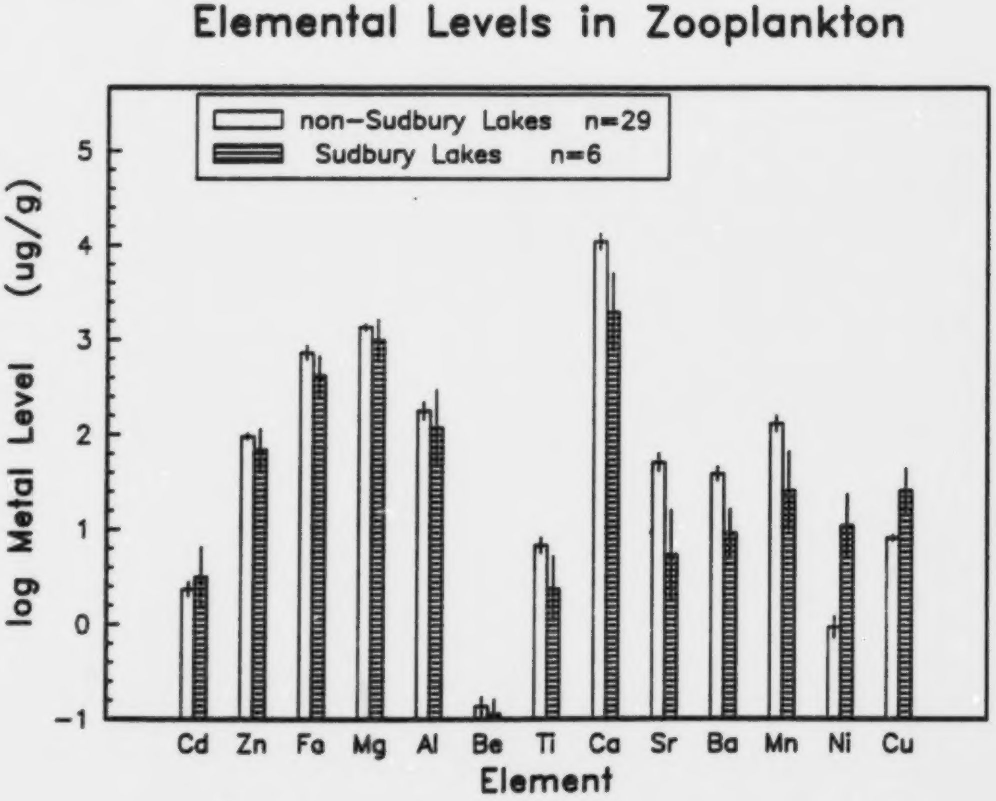
Fig. 13. Relationship between Cd levels in zooplankton and the cyclopoid biomass (as proportion of total biomass) in Plastic Lake (based on 1985 and 1986 data).

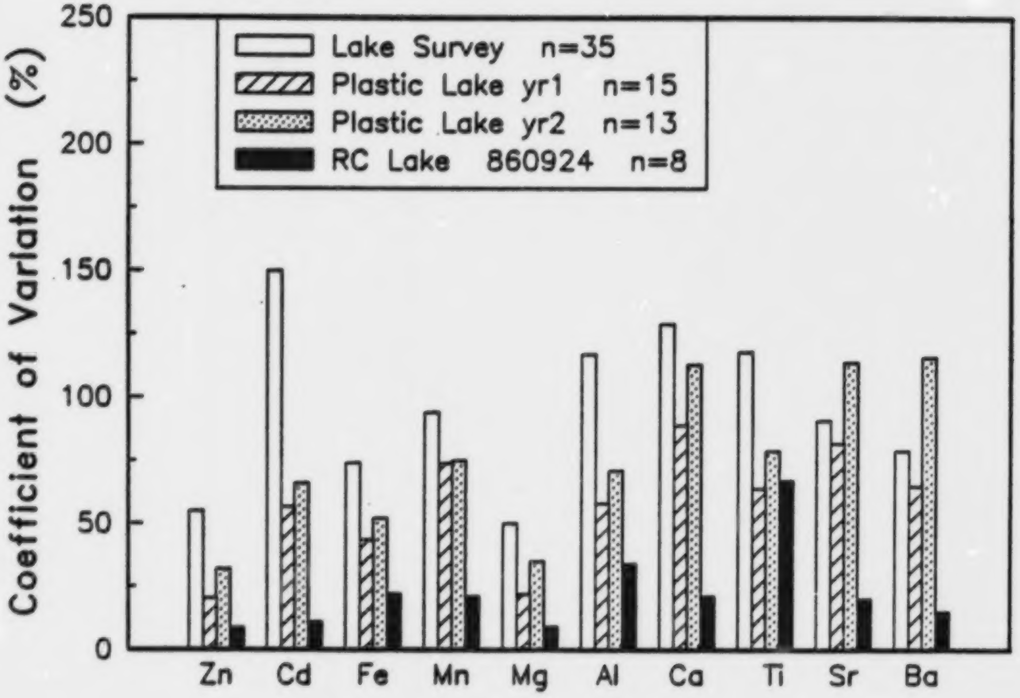
Fig. 14. Relationship between Al levels in zooplankton and the cyclopoid biomass (as proportion of total biomass) in Plastic Lake (based on 1985 and 1986 data).


ALGONQUIN PROVINCIAL PARK
GEORGIAN BAY
N
DORSET
PLASTIC
LAKE

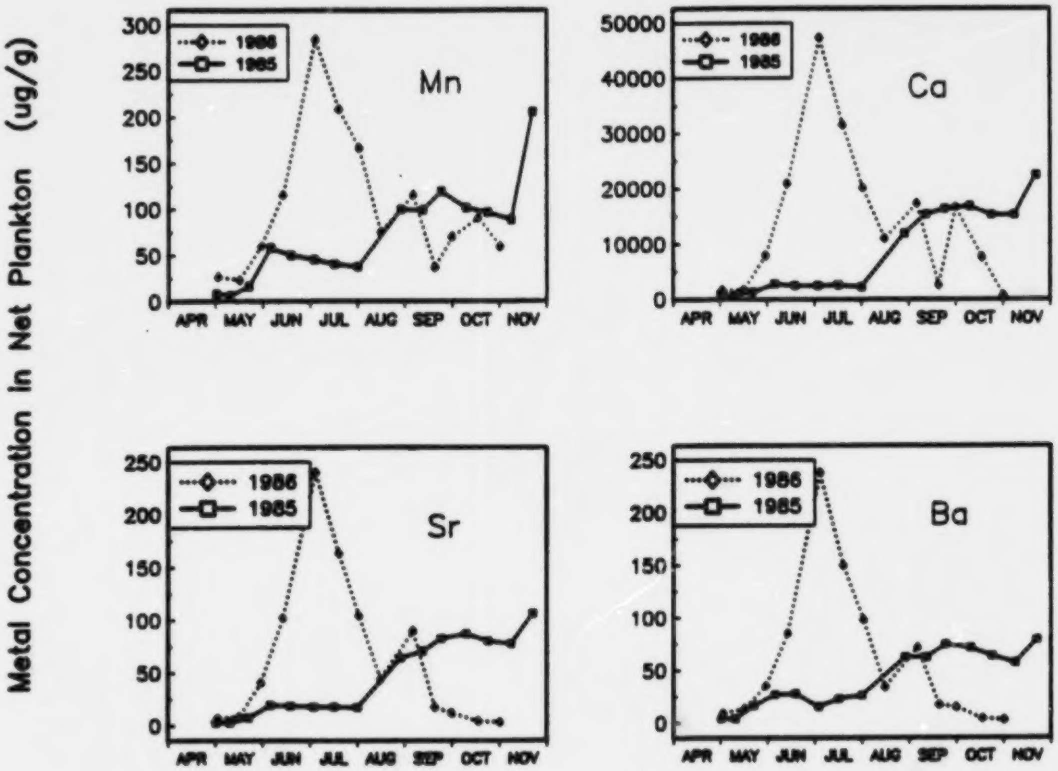


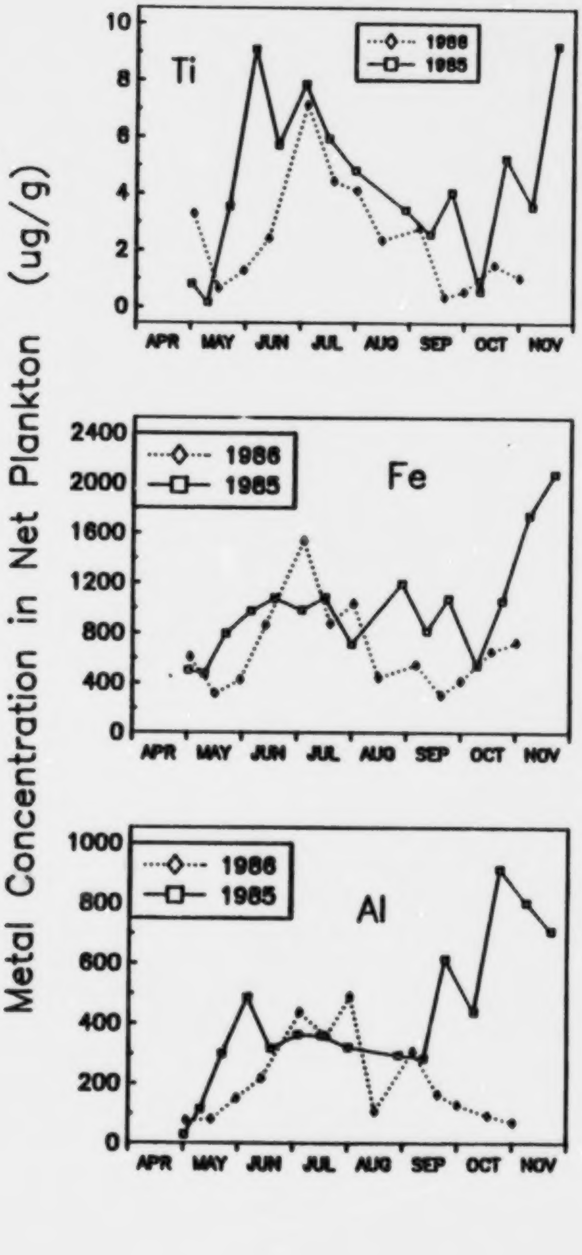
NBS Oyster Tissue Comparison

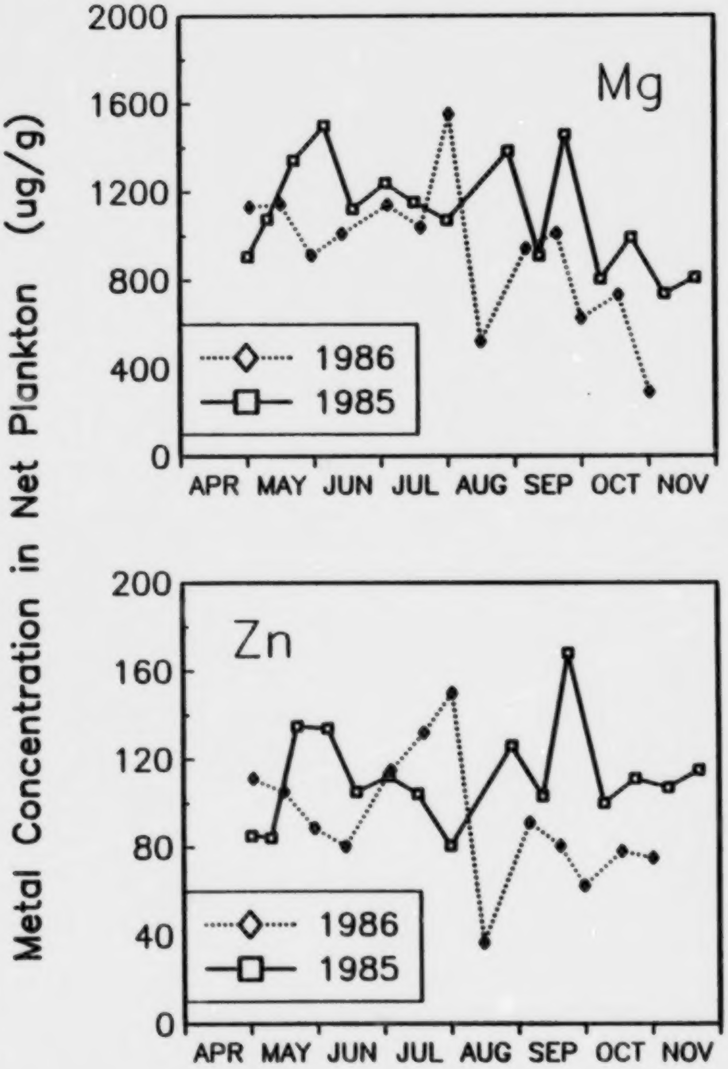

Elemental Levels in Zooplankton

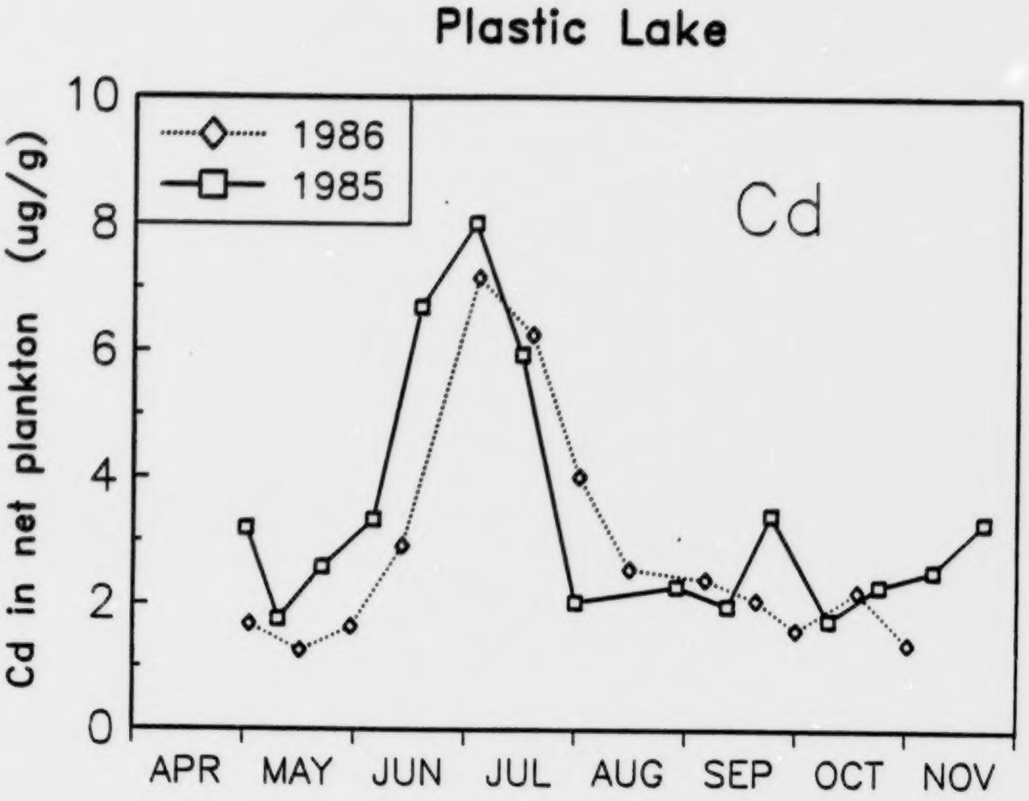


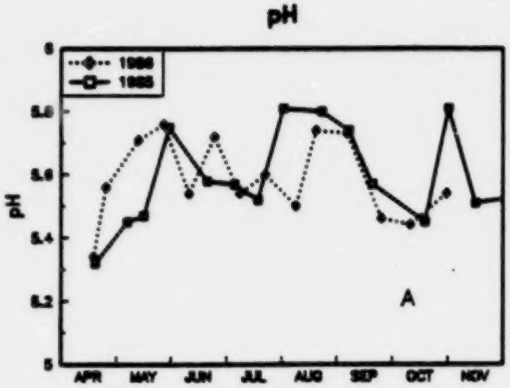
Sources of Variance in Zooplankton Metal Data
Lakes, Time and Space

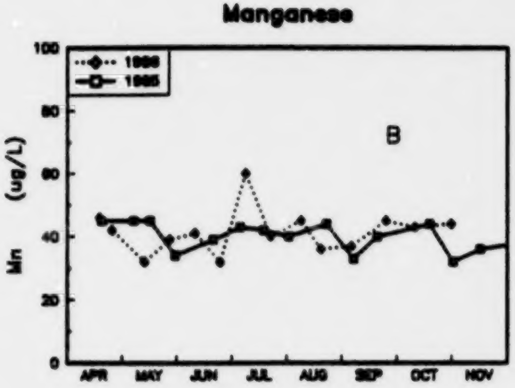

Metal Concentration In Net Plankton (ug/g)
1986
1985
Mn
Ca
Sr
Ba
0
50
100
150
200
250
300
10000
20000
30000
40000
50000
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV

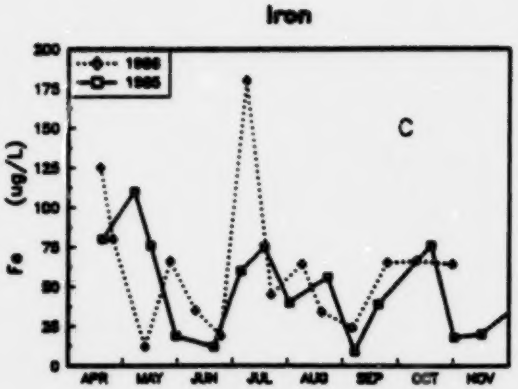

Metal Concentration in Net Plankton (ug/g)
Ti
1986
1985
0
2
4
6
8
10
Fe
0
400
800
1200
1600
2000
2400
Al
0
200
400
600
800
1000
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV

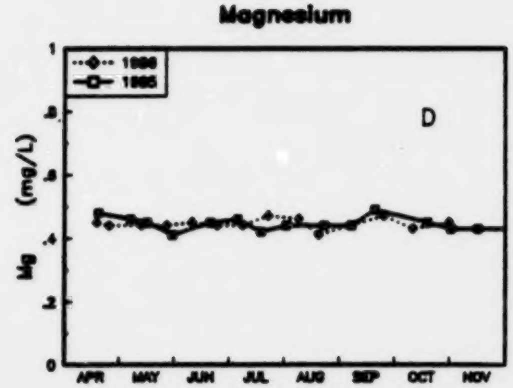

Metal Concentration in Net Plankton (ug/g)
Mg
2000
1600
1200
800
400
0
1986
1985
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
Zn
200
160
120
80
40
0
1986
1985
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV

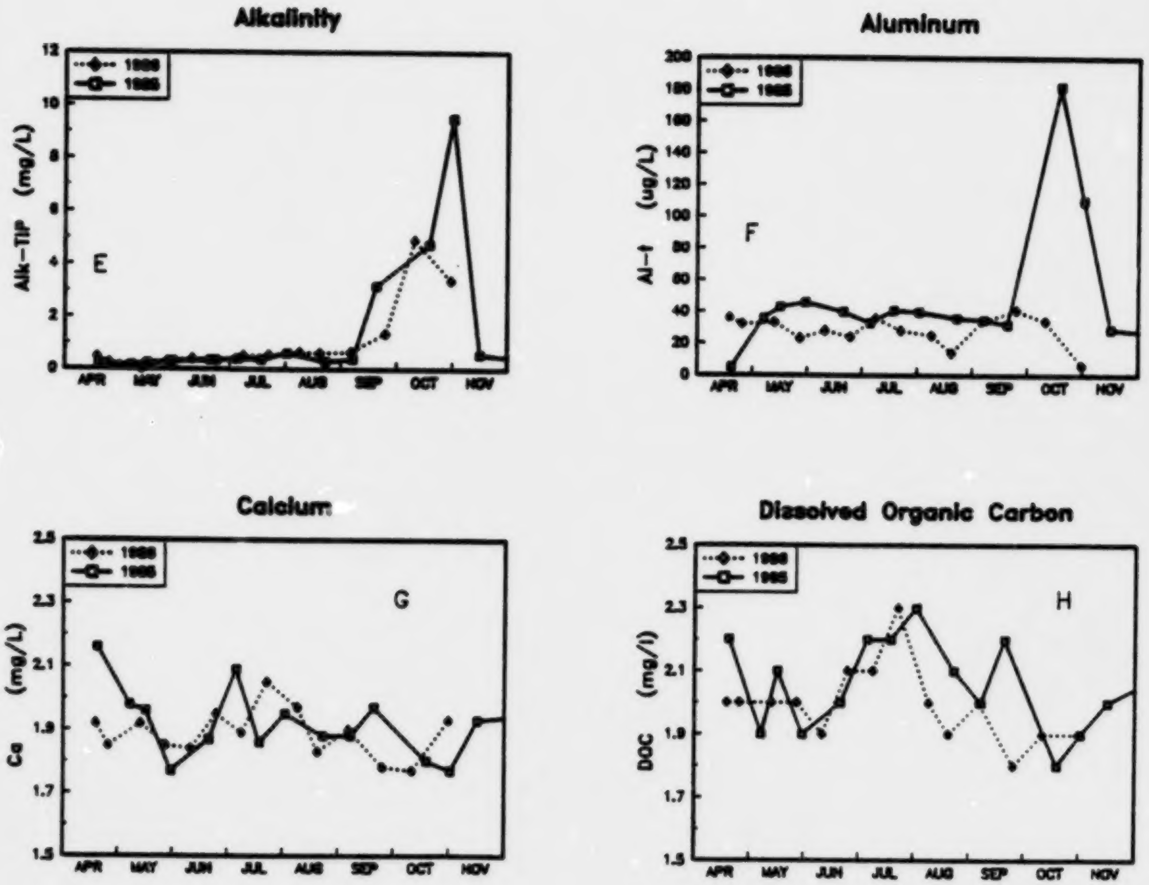

Plastic Lake
1986
1985
Cd
Cd in net plankton (ug/g)
0
2
4
6
8
10
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV

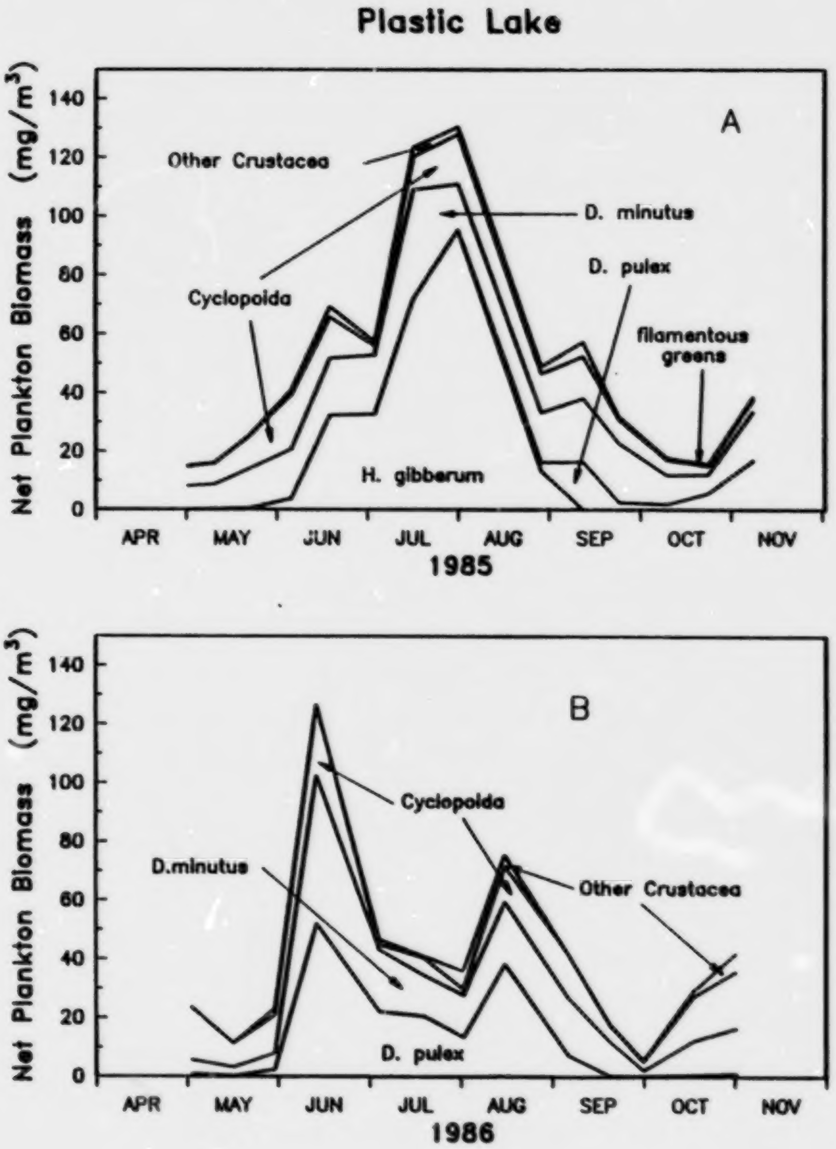

pH

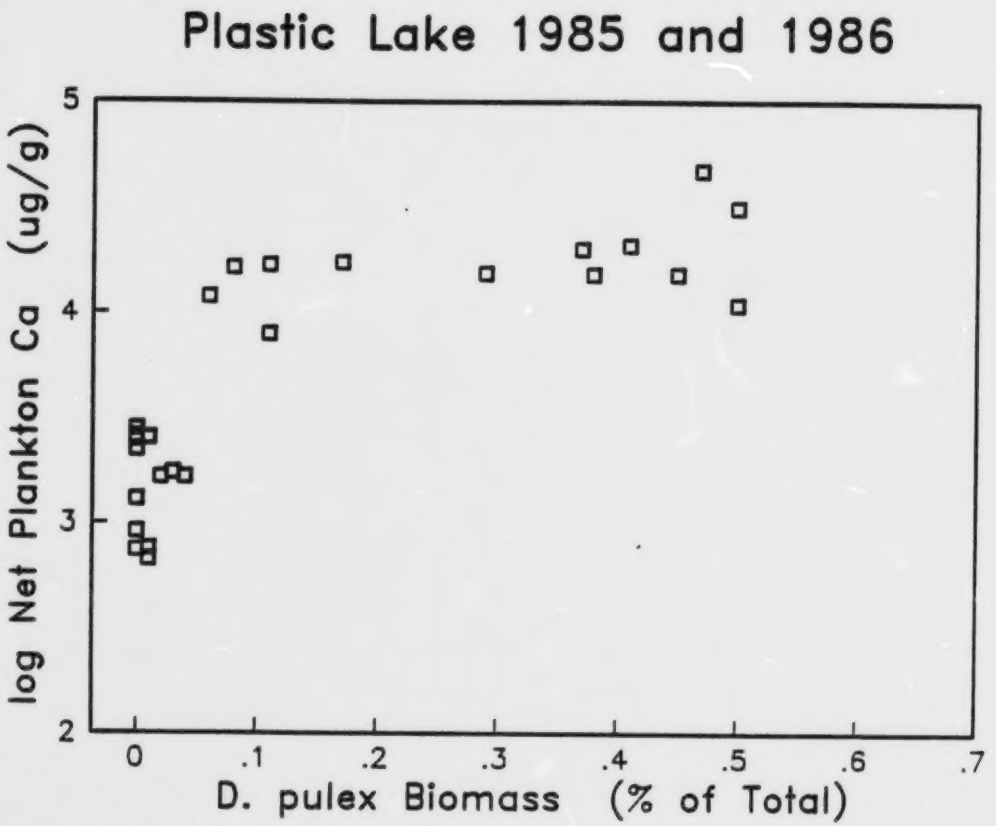

Manganese

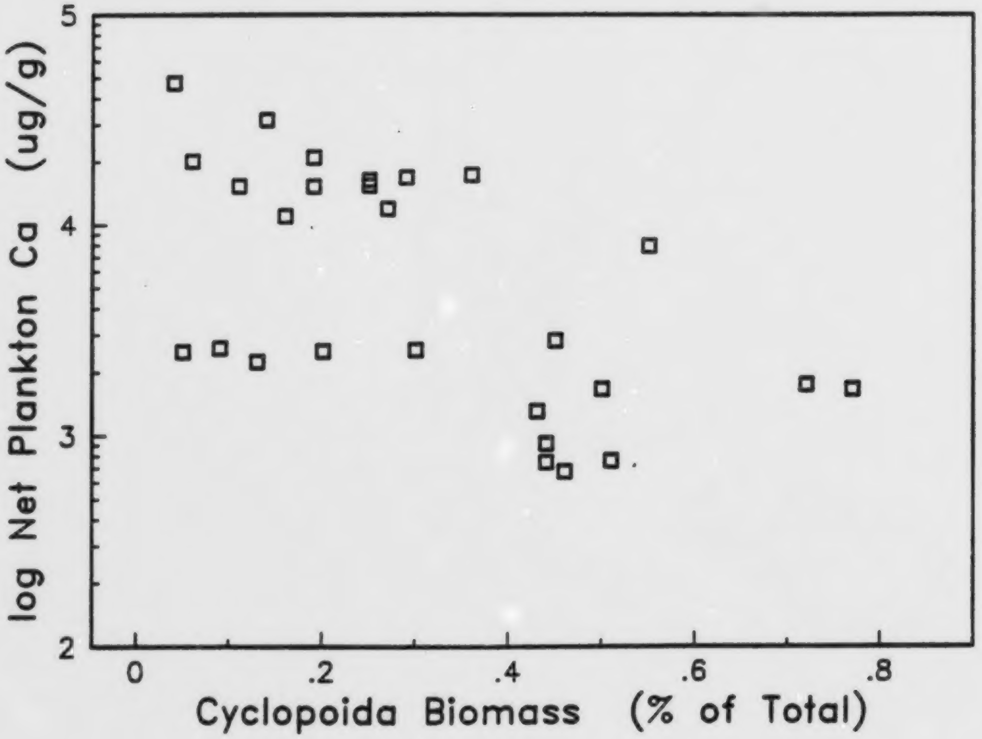

Iron


Magnesium

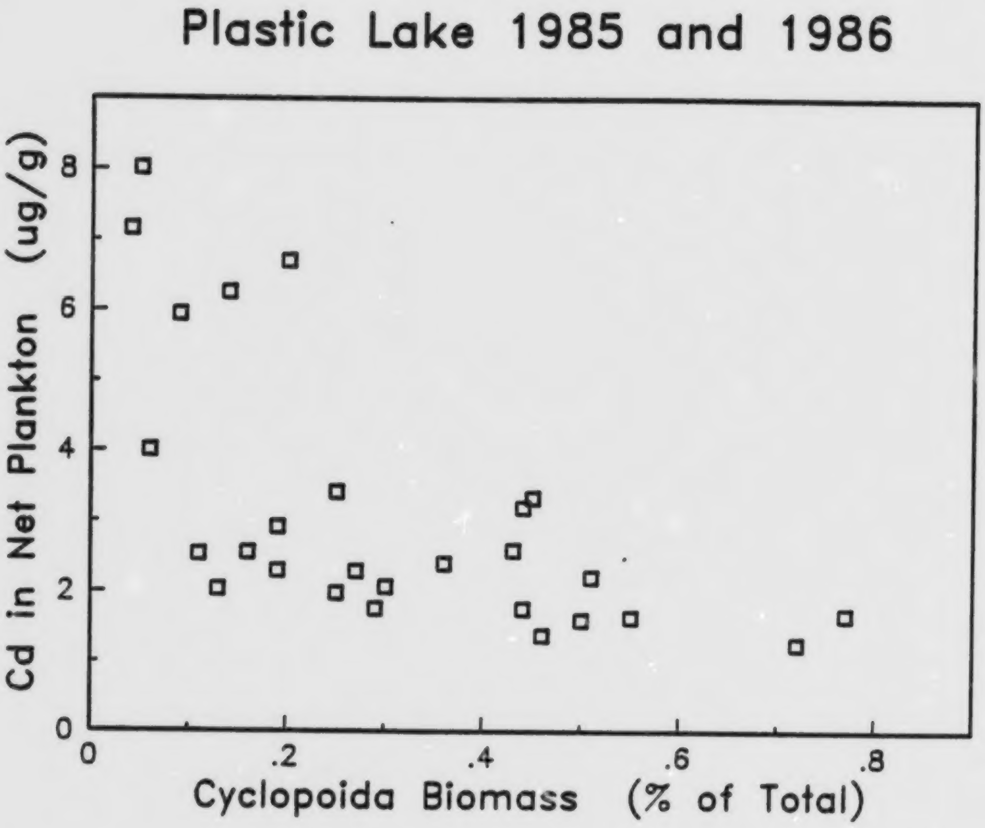

Alkalinity
1986
1985
Alk-TIP (mg/L)
12
10
8
6
4
2
0
E
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
Aluminum
1986
1985
Al-t (ug/L)
200
180
160
140
120
100
80
60
40
20
0
F
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
Calcium
1986
1985
Ca (mg/L)
2.5
2.3
2.1
1.9
1.7
1.5
G
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
Dissolved Organic Carbon
1986
1985
DOC (mg/l)
2.5
2.3
2.1
1.9
1.7
1.5
H
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV

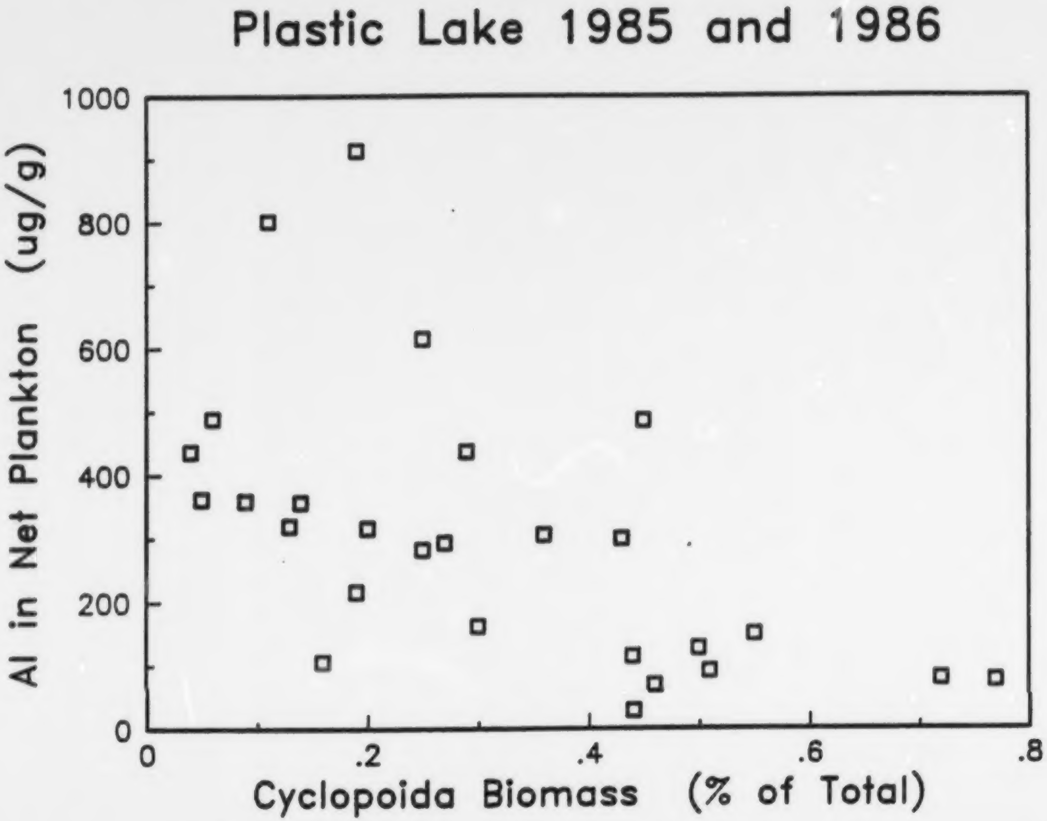

Plastic Lake
A
Net Plankton Biomass (mg/m^3)
0
20
40
60
80
100
120
140
Other Crustacea
D. minutus
D. pulex
Cyclopoida
filamentous greens
H. gibberum
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
1985
B
Net Plankton Biomass (mg/m^3)
0
20
40
60
80
100
120
140
Cyclopoida
D.minutus
Other Crustacea
D. pulex
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
1986


Plastic Lake 1985 and 1986
log Net Plankton Ca (ug/g)
5
4
3
2
0
.1
.2
.3
.4
.5
.6
.7
D. pulex Biomass (% of Total)



Plastic Lake 1985 and 1986


Plastic Lake 1985 and 1986
Cd in Net Plankton (ug/g)
0
2
4
6
8
0
.2
.4
.6
.8
Cyclopoida Biomass (% of Total)


Plastic Lake 1985 and 1986
Al in Net Plankton (ug/g)
1000
800
600
400
200
0
0
.2
.4
.6
.8
Cyclopoida Biomass (% of Total)

AVAILABILITY OF ZINC TO BENTHIC ORGANISMS FROM SEDIMENT FRACTIONS

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Toronto, Ontario
December 1987

INTRODUCTION

Zinc of industrial origin is substantially elevated in recently deposited sediments of the nearshore zone of the Great Lakes (Fitchko and Hutchinson, 1975; Konasewich et al., 1978; Persaud et al., 1985), as well as lakes in southern Ontario (Evans et al., 1983). The toxicity of zinc to aquatic biota is well documented (Brungs, 1969; Spehar, 1976; Chapman, 1978; Pierson, 1981; Anderson et al., 1980; Brkovic-Popovic and Popovic, 1977; Forstner and Wittmann, 1981; Attar and Maly, 1982). Since benthic deposit-feeders are known to accumulate zinc and other heavy metals from ingestion of sediment (Luoma and Jenne, 1976; Bryan and Hummerstone, 1978; Luoma, 1983), it is of considerable importance to determine how much of this recently deposited zinc can be assimilated by benthic organisms and transferred to fish and other organisms higher in the food chain.

Availability of trace metals to benthic deposit-feeders is intimately dependent upon the physical-chemical forms in which the metals are present in the sediments (Luoma and Jenne, 1976a, b; Bryan and Hummerstone, 1977; Bryan and Uysal, 1978; Luoma and Bryan, 1978; Luoma, 1983; Tessier et al., 1984). In most studies, attempts have been made to correlate the heavy metal contents of deposit-feeding macrofauna with a particular operationally defined chemical fraction or fractions of the metal in the sediments. The ultimate goal of these studies is to find a universal predictor of the metal content of benthic invertebrates. Thus, Luoma and Bryan (1978) related the lead content of the bivalve Scrobicularia in a British estuary to the ratio of Pb/Fe in the sediments extracted with 0.1 N HCl. Luoma and Jenne (1976a, b) labelled natural and artificial sediments with heavy metal radioisotopes and found good correlations between uptake of zinc-65 and cadmium-109 in the deposit-feeder Macoma balthica with readily-exchangeable zinc-65 and ethanol-extracted cadmium-109 respectively in the sediments. Luoma and Bryan (1979) related the zinc content of the bivalve Scrobicularia to easily-exchangeable zinc in British estuarine sediments. In the same study, the zinc content of the bivalve Macoma balthica from San Francisco Bay was related to the ratio of oxide-bound iron divided by easily exchangeable manganese and organic carbon in the sediments. Tessier et al. (1984) related the copper concentration in the bivalve Elliptio (actually a filter feeder) to the ratio of Cu (exchangeable + carbonate-bound + Fe/Mn oxide-bound) to oxide-bound iron in freshwater sediments.

In this study we present an alternative method for determining the bioavailability of heavy metals in aquatic sediments that involves labelling sediments with a heavy metal radionuclide. When a benthic deposit-feeder feeds on sediments containing a heavy metal and an analogous radioisotope, the specific activity of the radioisotope in the organism should approach the specific activity of the radioisotope in the biologically available fraction(s) of the sediments (Ophel, 1963; Ophel and Fraser, 1971). In this context, specific activity is defined as the ratio of zinc-65 activity per gram of sediment or animal to micrograms of zinc per gram. Measurements of the specific activity in the organisms and in chemical fractions of the sediment, therefore, replace correlations between total body content and concentration in each chemical fraction as a method of determining which fraction serves as a source of the metal to the organisms.

Measurements of specific activity were also used to trace the movement of recently added zinc through potentially bioavailable sediment fractions. This work follows that by Andrews et al. 1985 who found that cobalt-60 is taken up initially and retained for months in the exchangeable and carbonate-bound fractions and hence is highly available to deposit-feeders. On the other hand, routine fractionation of the sediments indicated that over 80% of the cobalt in these sediments was in a residual or oxide-bound fraction, presumeably unavailable to deposit-feeders. There was, therefore, a non-proportional distribution of the newly added cobalt between the chemical fractions of this metal in the sediments.

The objectives of this study were as follows:

1. to identify the sediment chemical fraction(s) serving as a source of zinc to benthic deposit-feeders;
2. to examine the vertical distribution of this/these sediment fractions in the sediments in relation to animal feeding behaviour; and
3. to examine the movement of recently incorporated zinc between sediment fractions with the aim of comparing its bioavailability with that of "aged" zinc measured in routine sediment fractionation of surface sediments.

METHODS

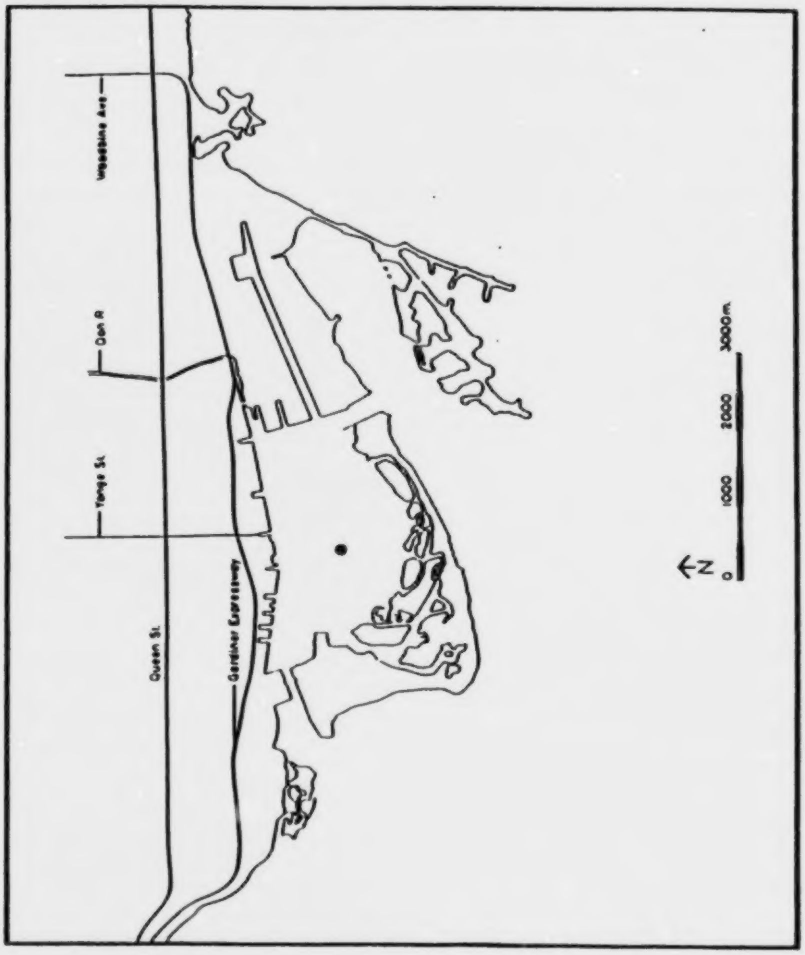
Source of Sediment-Bound Zinc to Benthic Deposit-Feeders

To determine which chemical fraction of the sediments serves as a source of zinc to benthic deposit-feeders, two species of oligochaetes, Tubifex tubifex and Limnodrilus hoffmeisteri were grown on Toronto Harbour sediments labelled with zinc-65. The activity and specific activity of zinc-65 in the organisms were then compared with those in chemical fractions of the sediments.

Three litres of surface sediments were collected from a selected station in Toronto Harbour by Ekman dredge (Figure 1). Thirty microcuries of inorganic zinc-65 were added to these sediments and allowed to equilibrate for three weeks. The sediments were continually stirred during this time to maintain oxic conditions. About 150 ml of this sediment were then added to each of 22 crystallizing dishes and covered with 2 cm of dechlorinated tap water. Ninety tubificid worms were then placed in each crystallizing dish of labelled sediments. Twelve dishes were devoted to Tubifex while eight were devoted to Limnodrilus. When added to the dishes, both species of tubificids quickly burrowed into the sediments and appeared to feed normally. The sediments were stirred about every week to prevent anoxia and the associated diagenetic changes.

Ten experimental dishes were sampled at one- and two-month intervals at which time two sediment samples (5 gm) and all the worms were taken from each dish. The sediment samples were subjected to a modified version of the sequential extraction procedure of Tessier et al. (1979) and the sediment-bound zinc was seperated into the operationally defined categories of: interstitial zinc, easily-exchangeable zinc, carbonate-bound zinc, Fe/Mn oxide-bound zinc, organically-bound, and residual zinc. Separate samples were also taken for total zinc. In all cases, the samples were treated wet rather than dry and ground, as drying and grinding the sediments dramatically change the metal partitioning (Chen et al., 1976; P. Campbell, pers. comm.). Total and residual zinc were analyzed by digesting the sediments in nitric acid at 95°C, rather than hydrofloric acid as described by Tessier et al. (1979). The chemical extracts were analyzed for total zinc by atomic absorption spectroscopy. Two mL of each extract were sent to Chemex Labs, Vancouver, for the analysis of zinc-65 by gamma spectroscopy using a highly shielded NaI(Tl) crystal detector.

Figure 1: Location of Sampling Station in Toronto Harbour ●


Woodbine Ave.
Don R.
Yonge St.
Queen St.
Gardiner Expressway
N
0
1000
2000
3000m

The worms from each experimental dish were extracted by sieving the sediments through a 75 um mesh net. They were then separated into groups of three and each group was then placed for 24 hours in glass scintillation vials containing 5 mL of dechlorinated tap water. This procedure was followed to allow the worms to evacuate their guts and avoid the clumping that is characteristic of larger groups of worms. Clumping of the worms prevents effective evacuation of the gut and encourages coprofagy. Failure to remove gut contents can result in substantial errors in measuring tissue concentration of heavy metals (Chapman, 1985; Bindra and Hall, 1977; Chapman et al., 1980; Elwood et al., 1976). Microscopic examination of the worms indicated that gut evacuation was complete.

The worms were then pooled into groups of 30 (three samples per dish) and dried at 50°C on preweighed, acid-washed plastic strips (2 cm^2). Each sample, consisting of 7 to 10 mg dry weight of worm material and the plastic strip, was digested in 2 mL of concentrated nitric acid at 90°C for four hours and then made up to 4 mL in volume with distilled, deionized water. Samples were analyzed both for total zinc and zinc-65. Blank analyses of the plastic strips indicated that they contributed negligable amounts of zinc to each extract.

In order to determine the quantity of zinc-65 adsorbed externally to the organisms, five samples of 30 Limnodrilus and five of Tubifex were exposed to 1 uCi of zinc-65 in 100 mL of dechlorinated tap water without sediments. During this time, no mortality was observed despite the absence of substrate and food. At the end of the week, the animals were removed, washed and placed in unlabelled dechlorinated water for 24 hours. The animals were then digested and analyzed as described above. Samples of the labelled water used in this experiment were also analyzed for zinc and zinc-65.

Bioavailability of Zinc with Sediment Depth

To evaluate the chemical partitioning and bioavailability of sedimentary zinc with sediment depth, two undisturbed cores from Station 1 in Toronto Harbour were sectioned under nitrogen at 1 cm intervals to a depth of 10 to 13 cm. Aliquots of sediment from each section were extracted for zinc by using the modified version of the sequential extraction procedure of Tessier et al. (1979). In addition, the first four extractions (interstitial, easily-exchangeable, carbonate-bound and Fe/Mn oxide-bound) were performed under nitrogen in sealable polycarbonate tubes. All reagents were stripped of oxygen by bubbling with nitrogen gas. A nitrogen atmosphere was maintained both in the sectioning of the cores and in their extractions to prevent the introduction of oxygen into the sediments. Changes in redox conditions are known to change the chemical partitioning of zinc in the sediments (Gambrell et al., 1980; P. Campbell, pers. comm.).

Exchange Potential of Zinc Between Sediment Fractions

The movement of zinc-65 through the chemical fractions of zinc in Toronto Harbour sediments was followed over the period of a month in order to determine relative rates of exchange of zinc between chemical fractions and the fate of small quantities of zinc added to the sediments. Surface sediments were kept stored and oxygenated for a month before the experiment. Two samples of sediment (150 ml) were then exposed to 2 microcuries each of zinc-65. Starting immediately after dosing and over a period of one month, 11 subsamples from each sediment sample were taken over logarithmically increasing periods of time and extracted as described above, to determine the chemical partitioning of both stable zinc and zinc-65. Both the activity and specific activity of zinc-65 in each chemical fraction were examined over the one-month period.

RESULTS AND DISCUSSION

Identification of the Bioavailable Fraction of Sedimentary Zinc to Tubificids

Zinc Content of Tubificid Worms

The mean zinc contents of worms exposed for one and two months to Toronto Harbour sediments were found to be quite similar at 256 and 259 ug/g respectively (Table 1). These values are three to four times higher than zinc concentrations in tubificids measured in other studies, reviewed by Chapman et al. (1980), but fall into the range of zinc levels in samples of biota (mostly tubificids) taken by the Ministry of the Environment in Toronto Harbour (Deo Persaud, pers. comm.) and those found for tubificids from Port Hope Harbour (Hart et al., 1986).

A large difference in zinc content was evident between the two worm species, *Tubifex tubifex* and *Limnodrilus hoffmeisteri*. (Table 1). The zinc content of *T. tubifex*

TABLE 1: MEAN CONCENTRATION OF ZINC, ZINC-65 AND THE SPECIFIC ACTIVITY OF ZINC-65 IN TUBIFICIDS EXPOSED TO WATER (CONTROL) AND SEDIMENTS LABELLED WITH ZINC-65[1]

No. of Samples	Species	Mean Zinc Content (ug/g)	Mean Zinc-65 Content (Bq/g)	Specific Activity (Bq/ug zinc)
Control (-Sediment)				
5	Limnodrilus	186±24	$(5.12 \pm 1.27) \times 10^5$	$(2.76 \pm 0.57) \times 10^3$
5	Tubifex	262±35	$(2.22 \pm 0.48) \times 10^5$	$(0.87 \pm 0.25) \times 10^3$
Overall Mean		224±49	$(3.67 \pm 1.77) \times 10^5$	$(1.81 \pm 1.08) \times 10^3$
One-Month Sediment Exposure				
12	Limnodrilus	194±22	303±87	1.56±0.40
18	Tubifex	297±35	395±144	1.32±0.45
Overall Mean		256±59	358±131	1.42±0.44
Two-Month Sediment Exposure				
10	Limnodrilus	229±57	274±98	1.17±0.38
5	Tubifex	319±47	319[2]	1.18[2]
Overall Mean		259±68	278±94	1.17±0.36

[1] Values expressed as mean ± 1 standard deviation

[2] Based on only one sample having a significant number of counts, therefore no estimate of standard deviation available

was almost 100 ug/g greater than Limnodrilus in both the control and experimental dishes. This difference between the two species was statistically significant (p less than 0.05) and, to our knowledge, has never been reported in the literature. The ecological significance of this difference is open to speculation on the relative tolerances of the two species to heavy metals.

Zn-65 Uptake by Tubificids

During the one-month exposure to Toronto Harbour sediments labelled with zinc-65, significant accumulation of zinc-65 was observed in all the worm samples for a mean accumulation of 358 Bq/g dry weight of worm (Table I). T. tubifex accumulated about 90 Bq/g more zinc-65 activity than L. hoffmeisteri but because of the higher zinc content in Tubifex, the specific activities were very similar at 1.32±0.45 and 1.56±0.4 Bq/ug zinc, respectively. The mean specific activity for both species was 1.42 Bq/ug zinc.

Because many of the large worms died during the two-month exposure, only six out of the ten experimental dishes had sufficient mass of worms on which to make significant measurements of total zinc and zinc-65 activity. Nevertheless, similar results were found here as in the one-month exposure. The mean accumulation of zinc-65 activity during the two-month exposures (278 Bq/g) and the mean specific activity (1.17 Bq/ug Zn) were close to those obtained in the one-month exposure. The results suggest that one month is sufficient time for equilibrium of the radioisotope between pools within the organism and the sediment.

The control experiment, in which the worms were exposed only to zinc-65 without sediment, gave very different results. Although the overall activity of zinc-65 was the same in both experimental and control dishes (approximately 293 Bq/mL), the control worms accumulated three orders of magnitude more zinc-65 than the experimental worms (Table I). Zinc activity in the worm samples in the controls ranged from 163,000 to 707,000 Bq/g of worm. Specific activities were also three orders of magnitude greater for a mean of 1.8×10^3 Bq/ug zinc.

Zinc and Zinc-65 in the Sediment Fractions

The sediment extracts from both the one- and two-month tubificid, exposures (Table 2) reveal a partitioning of zinc similar to that in fresh sediment cores (see below). Less than 1% of the sediment-bound zinc is found in the easily exchangeable fraction, while approximately 80% is found in the Fe-Mn oxide-bound and carbonate bound fractions. Only minor quantities of zinc were found in the organic (6%) and residual (9 to 13%) fractions. The two experiments differed only slightly in zinc partitioning. Sediments from the two-month exposure had a slightly higher percentage of carbonate-bound and residual zinc and a lower percentage of Fe-Mn bound zinc. These differences could be due either to sediment heterogeneity or diagenetic changes occurring during the additional month.

The six chemical fractions in both experiments accumulated very different quantities of zinc-65 (Table 3). The carbonate-bound fraction picked up the largest amount of zinc-65 with an activity of 481 Bq/g in both experiments, while the easily exchangeable accumulated the smallest amount of zinc-65 at less than 20 Bq/g. The distribution of zinc-65 between fractions was disproportional to the amount of zinc in each fraction. The Fe-Mn bound fraction, for example, contained more than twice the amount of zinc than the carbonate-bound fraction, yet less than half the amount of zinc-65 activity. The degree of labelling in each fraction is expressed by the specific activity.

Comparison of Specific Activities of Zinc-65 in the Sediments and the Tubificids

Comparison of zinc-65 activity in the animals (Table 1) with zinc-65 activity in the sediment fractions (Table 3) shows that the Fe/Mn oxide fraction is closest in specific activity to that of the tubificid worms. The mean specific activity of the worms was 1.42 and 1.17 Bq/ug zinc respectively for the two exposures compared with 1.02 and 1.07 Bq/ug zinc for the specific activities of the Fe/Mn oxide-bound fraction of the sediments. In both experiments the Fe/Mn fraction is the only sediment fraction whose mean specific activity falls within one standard deviation of the specific activity of zinc-65 in the worms.

The similarity in specific activity of zinc-65 in the tubificids with that in the Fe/Mn oxide-bound fraction suggests that this metal fraction serves as a source of zinc to the

TABLE 2: CHEMICAL FRACTIONATION OF ZINC IN CHEMICAL FRACTIONS OF SEDIMENTS USED IN TUBIFICID EXPOSURES

Fraction	1	2	3	4	5	6*	7
One-Month Exposure							
Zinc (ug/g)	0.2	100	211	22	33	0.05	393
Percent of Total**	0.1	27.4	57.5	6.0	9.0	-	-
Two-Month Exposure							
Zinc (ug/g)	1.5	152	168	28	56	0.052	392
Percent of Total**	0.4	37.6	41.4	6.9	13.7	-	-

Fraction 1 = easily-exchangeable; 2 = carbonate; 3 = Fe/Mn oxide; 4 = organic; 5 = residual; 6 = interstitial; 7 = total. Values averaged over 11 dishes of two replicates each.

* Concentration expressed in mg/L.

** Percent expressed as the sum of the fractions.

TABLE 3: MEAN ACTIVITY (Bq/g) AND MEAN SPECIFIC ACTIVITY (Bq/ug zinc) OF ZINC-65 IN CHEMICAL FRACTIONS OF SEDIMENTS USED IN TUBIFICID EXPOSURES (Fraction 1 = easily-exchangeable; 2 = carbonate-bound; 3 = Fe/Mn oxide; 4 = organic; 5 = residual; 6 = interstitial)[1]

Fraction	1	2	3	4	5	6[2]
One-Month Exposure						
Activity	2.47±0.75	481±55	218±60	11.5±7.7	5.33±4.66	0.38±0.47
Specific Activity	12.6±7.8	4.96±0.9	1.02±0.16	0.446±0.291	0.158±0.142	4.6±1.7
Two-Month Exposure						
Activity	16.8[3]	481±96	179±48	17.3±1	17.4±16	1.6±0.87
Specific Activity	15.1	3.17±0.52	1.07±0.29	0.64±0.39	0.32±0.27	26.4±21.3

[1] All values expressed as mean ± one standard deviation

[2] Activity expressed as Bq/mL.

[3] Preliminary results only.

worms. Iron and the Fe/Mn oxide bound fraction of the sediments have been implicated in numerous studies on the bioavailability of trace metals to deposit-feeders (Luoma and Jenne, 1976a, Luoma and Bryan 1978, 1979; Tessier et al., 1984). These studies suggest that the iron-oxide bound fraction serves directly as a source of heavy metals or that iron competes with the organism for available metals. By using a very different technique, this study confirms the involvement of iron and Fe/Mn oxides in the bioavailability of heavy metals to benthic deposit feeders. Unlike some of the studies above, however, this study points to the Fe/Mn oxide fraction as a direct source of zinc to the organisms rather than a competitor with the organisms for available zinc.

This isotopic method of determining bioavailable fractions in sediments involves several assumptions which must be discussed. First, the method assumes isotopic equilibrium between the bioavailable(s) fraction and the organism. The actual length of time required for isotopic equilibrium between the sediments and these tubificid worms is uncertain. The literature, based largely on polychaetes and deposit-feeding clams, presents a wide range of times required for equilibrium and, to complicate matters, suggests that different pools exist in deposit feeders having different turnover rates of heavy metals (Renfro and Benayoun, 1976, Renfro et al., 1975). Renfro (1973) exposed the marine polychaete Hermione to zinc-65 labelled sediment and found that 60 days or more were required for this worm to approach steady-state with zinc-65 in the sediments. Luoma and Jenne (1976a), however, found that after eight days cadmium-109 uptake by the deposit-feeding clam Macoma balthica was solely the result of uptake from the solute pool of cadmium-109. In this study, we attempted to be conservative and assumed equilibrium between isotopic pools required at least 30 days and possibly 60 days. The data indicate that a 30-day exposure would have been sufficient. The oligochaetes did not increase in either zinc-65 activity or specific activity between the two exposures. The mean activities of the worms in the 30- and 60-day exposures are, in fact, quite close at 338 and 278 Bq/g worm respectively (Table 1).

Another assumption requiring discussion is that sediment ingestion is the dominant method by which tubificids accumulate zinc and zinc-65. Uptake of heavy metals labels directly from solution by benthic deposit feeders has been demonstrated in many studies, including those of Luoma and Jenne (1976a, 1977). Dean (1974) found that tubificids accumulated zinc-65 directly from water (without sediments), but not from labelled sediments. Prosi (1981) suggested that interstitial cadmium was a dominant source of this metal to Tubifex grown in Rhine River sediments. Many other studies, however, indicate the importance of particulate-bound metals in their accumulation by benthic deposit-feeders. Bryan and Hummerstone (1978) and Bryan and Uysal (1978) found that large proportions of most metals were concentrated in the digestive glands of deposit-feeding bivalves, a fact implying that they are chiefly absorbed from ingested sediment.

The control experiment in this study indicates that tubificids can indeed take up large quantities of metals (in this case zinc-65) directly from solution. Examination of the data, however, reveals that the mechanism of zinc-65 uptake in the controls is very different from that in the experimental dishes containing sediments. A plot of zinc-65 activity vs. the zinc content in the experimental worms (Figure 2A) produces a significant positive correlation where the slope is equivalent to a mean specific activity of the accumulated zinc-65. These results are consistent with a bioaccumulation model in which the specific activity of the worms approaches that of a bioavailable chemical fraction in the sediments. A similar plot for the control samples (Figure 2B) reveals a significant negative correlation, a finding indicating a very different mechanism of uptake.

It is likely that the mechanism of zinc-65 uptake by the control worms is that of adsorption to the external cuticle. Evidence for this can be seen in a plot of uptake of zinc-65 (Bq/g) in Limnodrilus vs. weight of the worms in each sample (Figure 3). Since each sample consisted of ten worms, the mass of the sample itself is proportional to the mass of an average worm in each sample. Because the surface area to volume ratio in the worms decreases with size, an inverse relationship would be expected for an adsorptive mechanism of uptake (Elwood et al., 1976). A significant inverse relationship does indeed exist for Limnodrilus, although no such relationship was evident with Tubifex.

While it is evident that in the absence of sediment particles, benthic deposit-feeders can adsorb large quantities of heavy metals directly from solution, it remains unclear whether adsorption or ingestion is the major mechanism of uptake in natural sediments. Although Prosi (1981) concluded that interstitial cadmium was the major source of this metal to Tubifex, bioconcentration factors, based on pore water for Tubifex grown in Rhine River and Lake Constance sediments were very different (1.8 and 0.3, respectively). Bioconcentration factors based on the whole sediments, however, were

Figure 2: Activity of Zinc-65 in Worms vs. Zinc Content of Worms in (A) One-Month Exposure and (B) Control

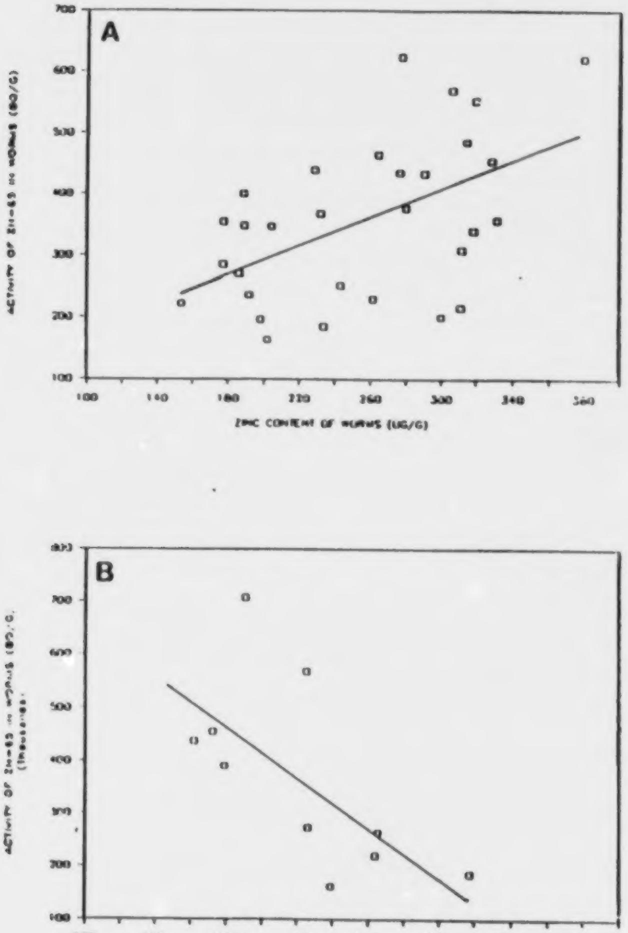
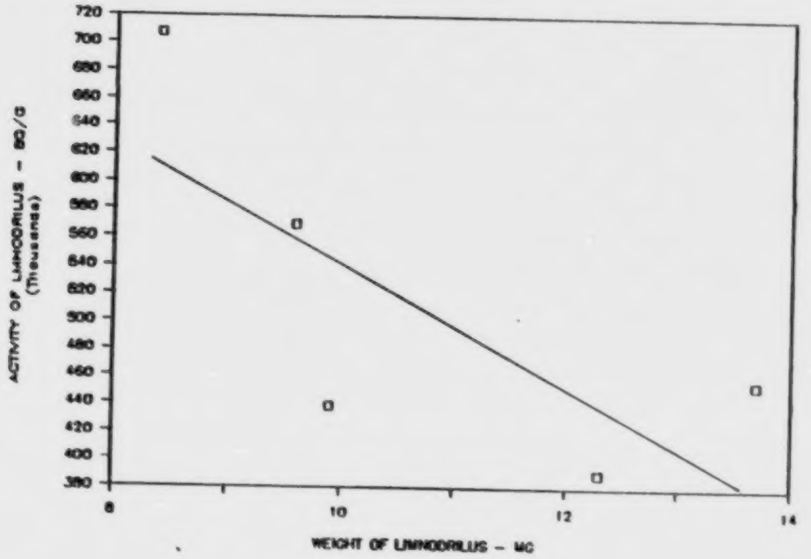


Figure 3: Activity of Zinc-65 in *Limnodrilus* in the Control Experiment vs. the Weight of the Worms



quite similar (7.34 and 7.71) despite very different levels of cadmium in the two sediments (5.48 and 0.35 ug/g). These calculations contradict his conclusions by suggesting that particle-bound rather than interstitial cadmium is the source of this metal to the worms. The control experiments and those of Dean (1974) represent an artificial situation in which organisms are exposed to zinc-65 in water without sediments. In nature, sediment particles would compete strongly with the organisms for the available zinc-65. While virtually all the added zinc-65 was available to the organisms in the control experiment, only 0.4% of zinc-65 added to Toronto Harbour sediments is associated with the interstitial water and hence available for adsorptive uptake by benthic oganisms (see later results). Conclusive determination of the mechanism of uptake of heavy metals by benthic deposit-feeders whether adsorptive or ingestive, will require further experimentation already underway. Until these results are available, we will assume that ingestion is the main mechanism of assimilation of heavy metals by deposit-feeding fauna.

Bioavailability of Sediment-bound Zinc with Sediment Depth

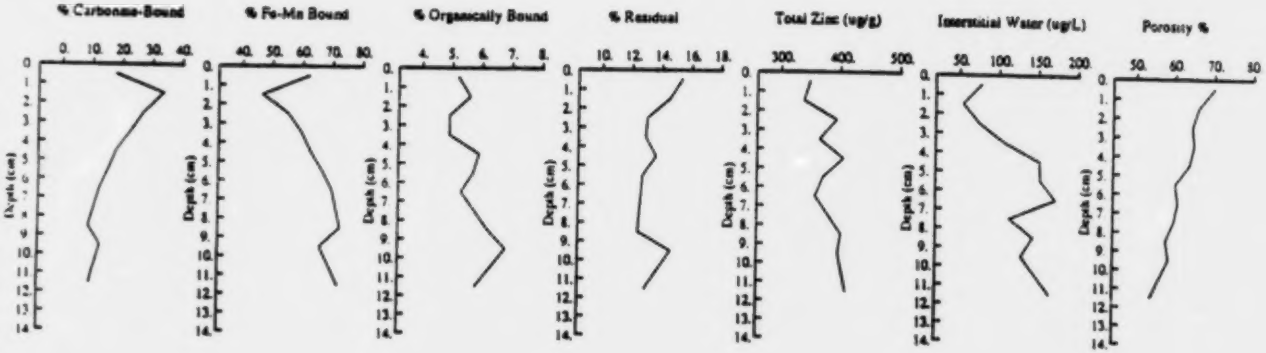
Chemical Fractionation of Zinc with Sediment Depth

In both cores from Toronto Harbour (Figure 4) porosity decreased from about 75% to 50% over 14 cm of depth. The smoother porosity profile in Core No. 1 suggests that this core is the less disturbed of the two, although both cores have probably been greatly influenced by harbour activities. Pore water concentrations of zinc range from 54 to 164 ug/L and appear to increase with depth in Core No. 1. This increase in depth is not apparent in the second core. The contribution of pore water to the overall concentration of zinc is very small. If we assume a sediment porosity of 75%, the interstitial and total zinc concentrations to be 150 ug/L and 400 ug/g respectively, the interstitial water only accounts for about 0.1% of the total sedimentary zinc. Almost all of the zinc, therefore, is bound to the particles.

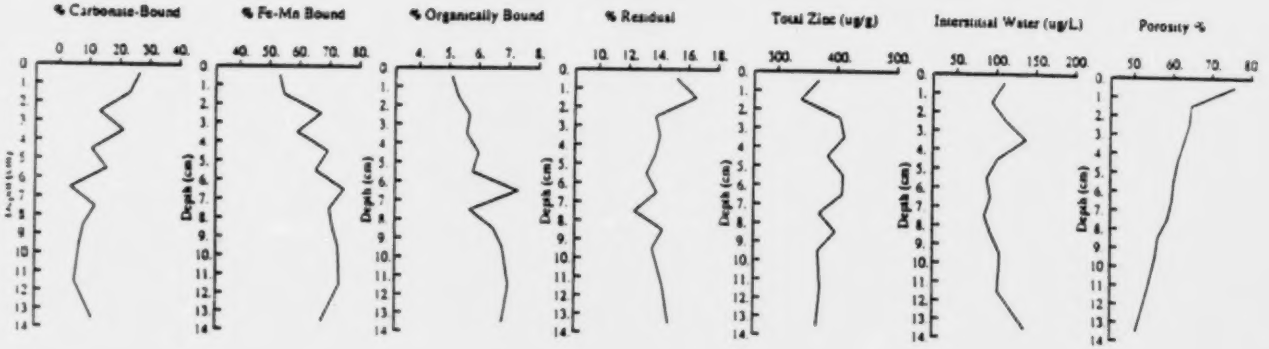
Total zinc in the cores, ranging from 350 to 450 ug/g, is high relative to background levels in nearshore zones of Lake Ontario (100 ug/g), but is well within range of zinc contents in river mouths and harbours (17 to 2,010 ug/g; Mudroch et al., 1986) and polluted river sediments in Europe (153 to 3,072 ug/g; Calmano and Forstner, 1983). The values in this study are comparable to those obtained in Toronto Harbour by Persaud et al. (1985). The increase of total zinc with depth in Core No. 1 was not observed in the

Figure 4: The Chemical Fractionation of Zinc in Two Cores From Toronto Harbour

Core 1



Core 2



second core or in the literature. Total zinc actually decreased with depth in two Norwegian lakes (Reuther et al., 1981) and in Lake Constance, Germany (Forstner, 1982; Forstner and Wittman, 1983).

Exchangeable zinc in the Toronto Harbour cores was below detection. The solution of Mg Cl_2 used for these extractions actually lost contaminant levels of zinc to the sediments, which acted in this case as a cation adsorber. In subsequent sequential extractions of Toronto Harbour sediments, an ultrapure grade of the salt was used, and measurable levels of easily-exchangeable zinc were obtained. Nevertheless, easily-exchangeable zinc was always less than 1.6% and frequently less than 0.2% of the total zinc content. Reuther et al. (1983) also found very low percentages of cation exchangeable zinc (1 to 6%) in cores from the two Norwegian lakes mentioned above. Similarly, low levels of exchangeable zinc were found by Calmano and Forstner (1983) in European rivers and by Rapin et al. (1983) in Mediterranean sediments (less than 3%). Tessier et al. (1979) also found levels of easily-exchangeable zinc below detection in sediments from the Yamaska and St. Francis Rivers, Quebec.

Most of the particle-bound zinc, about 80%, resides in the carbonate-bound (13 to 17%) and Fe/Mn oxide-bound fractions (63 to 67%). Similarly, high levels of zinc were found in analogous chemical fractions of sediments extracted in the studies mentioned above (Forstner, 1982; Calmano and Forstner, 1983; Rapin et al., 1983; Ruether et al., 1983). Carbonate-bound zinc in Core No. 1 increases for the first 2 cm then decreases over the length of the core. A similar subsurface maximum in this chemical fraction was observed for zinc in Lake Constance sediments (Forstner, 1982) and for cobalt in sediments from the Ottawa River (Andrews et al., 1983). This decrease in carbonate-bound metals with depth in the sediments is probably caused by a parallel decrease in pH that results in a dissolution of carbonate compounds. The subsurface maximum is less easily explained. In the Ottawa River sediments, low levels of carbonate-bound cobalt near the sediment surface were associated with high levels of easily-exchangeable cobalt. The latter fraction may compete with the carbonate compounds for the metal. A similar trend in easily-exchangeable zinc was not evident in the cores from Toronto Harbour. Moreover, a subsurface maximum in carbonate-bound zinc did not occur in the second core.

The Fe/Mn bound zinc increased with depth in both Toronto Harbour cores. This increase from about 50 to 70% of the particle-bound zinc seems to correspond well with the decrease in carbonate-bound zinc. It seems that these two fractions virtually control the overall partitioning of the metals in the sediments. Slight chemical or diagenetic changes with depth result in the transfer of metal from one of the two fractions to the other, while significant transfer of zinc to other fractions does not appear to occur.

Of the remaining fractions, organically-bound zinc increases slightly with depth, from about 5 to 7%, while no trends are apparent in the 14 to 16% of the sediment-bound metal classified as residual and extracted only in hot nitric acid.

Implications for Benthic Deposit-feeders

The chemical fractionation of zinc with sediment depth (Figure 4) has important implications for the ultimate accumulation of zinc by benthic oligochaetes. Figure 4, indicates that over the upper 10 cm of sediments between 50 and 70% of the metal is found in the Fe/Mn oxide bound fraction. This means that in general 50 to 70% of sediment-bound zinc is available to tubificids.

The exact quantity of available zinc will, of course, depend on the feeding habitats of the worms and their vertical distribution in the sediment column relative to that of the Fe/Mn oxide-bound zinc fraction. Studies by Brinkhurst et al. (1969), Milbrink (1973) and Krezoski et al. (1978) suggest that the majority of oligochaetes are found in the uppermost 6 cm of sediment. Krezoski et al. (1978) studying sediments from Lake Huron similar to ours found that most of the oligochaetes were in the 0 to 5 cm interval. None were below 10 cm. Based on these results, we expect the majority of the worms to be exposed to bioavailable levels of zinc between 45 to 65% of the total zinc content of the sediments (We are using the less disturbed Core No. 1 for these calculations). Since tubificids normally feed at depth and deposit their feces on the sediment surface, they are likely to ingest sediments having levels of bioavailable zinc towards the higher extreme of this range.

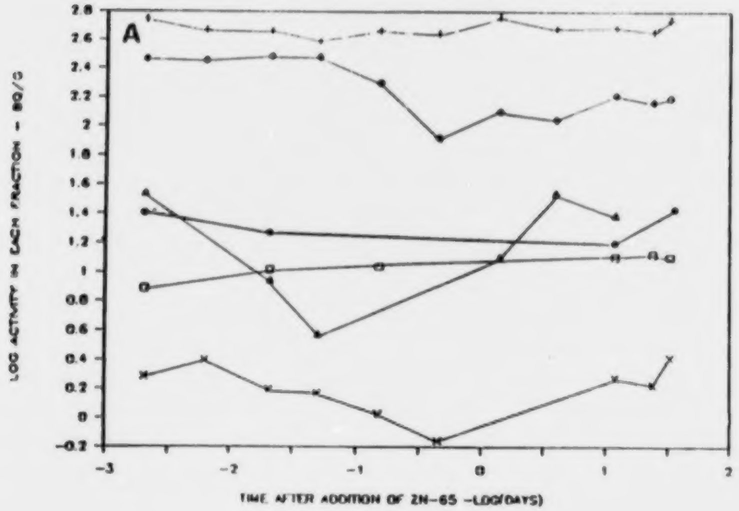
Relative Exchange Potential of Zinc in Chemical Fractions of Toronto Harbour Sediments

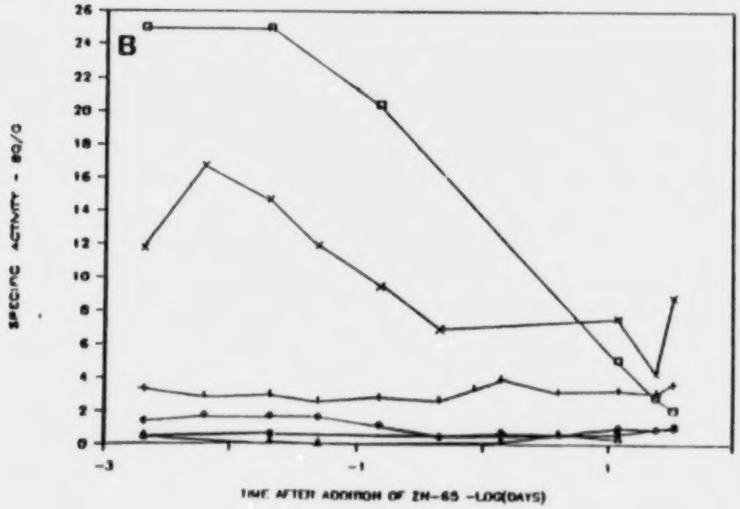
When added to Toronto Harbour sediments, inorganic zinc-65 was rapidly taken up almost exclusively by the sediment particles. Within three minutes after dosing, over 99% of the zinc-65 was associated with the particulate fraction and only 0.4% with the interstitial water. Most of the zinc-65 goes directly into the carbonate-bound (65%) and the Fe/Mn oxide-bound (30%) fractions. Much smaller quantities are taken up by the exchangeable fraction (0.8%), residual fraction (4%), organic fraction (2.5%) and interstitial water (less than 0.4%). Figure 5A, showing mean activity in each fraction versus time, indicates that, over the month-long experiment, there is little net change in zinc-65 activity in each chemical fraction or exchange of the isotope between sediment fractions. Fluctuations in activity, such as those occurring in the residual and interstitial fractions, are caused primarily by the low counting rates and high statistical variability of these samples. The decrease in activity in the Fe/Mn oxide fraction at 36 and 10.8 days into the experiment represents an artifact caused by a drop in counting efficiency for this series of samples. The true behaviour of this fraction is probably like that of the carbonate-bound fraction where little change in activity occurs during the experiment.

Examination of the specific activity of zinc-65 in each fraction with time (Figure 5B) reveals that zinc-65 was not taken up in proportion to the size of each chemical fraction. Thus, the easily-exchangeable and interstitial fractions, together containing less than 2% of the total sediment-bound zinc, were the most heavily labelled fractions, with initial specific activities of 25 and 11.8 Bq/ug zinc. In comparison, the carbonate and Fe/Mn oxide-bound fractions, having over 80% of the total sedimentary zinc, took up proportionally less of the label, with mean-specific activities of only 3.33 and 1.39, respectively. The organic and residual fractions accumulated the least proportional amounts of zinc-65, with initial specific activities of 0.60 and 0.51 respectively.

The dramatic decrease in specific activity of the easily-exchangeable fraction is directly related to diagenetic changes during the course of the experiment. Between 4 and 12 days, easily-exchangeable zinc increased by an order of magnitude, from about 0.5 ug/g to 5.0 ug. This movement of zinc represents a shift of only 1.5% of the total zinc content of the sediments, and may be due to an increasing anoxia within the sediments. Presumably, the zinc came from a fraction such as the carbonate-bound fraction, where the specific activity was lower than in the easily-exchangeable fraction. The result of this shift was a dilution of the zinc-65 with stable zinc and a decrease in the specific activity of the easily-exchangeable fraction. A similar decrease in specific activity of the interstitial zinc fraction can also be partially attributed to a two-fold increase in interstitial zinc during the month-long experiment.

Figure 5: Activity (A) and Specific Activity (B) of Zinc-65 in Chemical Fractions of Toronto Harbour Sediments vs. the Time After Addition of Zinc-65. (+) carbonate; (◇) Fe/Mn oxide; (△) residual; (X) interstitial; (□) easily-exchangeable; (•) organic





Based on these measurements of specific activity in Figure 5B, it is possible to indicate the relative ease of exchange of zinc between each chemical fraction of the sediments and a hypothetical pool of free zinc. The relative order in decreasing magnitude is as follows:

- exchangeable zinc,
- interstitial zinc,
- carbonate-bound zinc,
- Fe/Mn oxide-bound zinc,
- organic zinc, and
- residual zinc.

The results of this study are similar to those obtained by Andrews et al. (1985). Adding cobalt-60 to natural sediments, these authors also found that little net exchange of cobalt-60 occurred between sediment fractions after the initial uptake. As in this study, they found that cobalt-60 was non-proportionally distributed between the chemical fractions. Both studies indicate that uptake and exchange kinetics determine the chemical distribution of heavy metals introduced to natural sediments. When a heavy metal is added to sediments, it will partition between the various chemical fractions in a manner dependent upon the kinetics of exhange between each fraction or between each fraction and a free form of the metal, perhaps in the interstitial phase. In the case of a metal and its analogous radionuclide, each chemical fraction of the sediments should approach the same specific activity if sufficient time is allowed, each fraction is equally accessible to the radionuclide and each exchange reaction is reversible.

Evidently, in these experiments and those of Andrews et al. (1985), these criteria for equilibrium were not met. The initial distribution of zinc-65 between chemical fractions, measured within minutes of its addition, is retained for the duration of the experiment (Figures 5A, 5B). This distribution, therefore, represents a meta-stable equilibrium. The time to reach true equilibrium is at least in the order of months, if not years.

The possibility of such a meta-stable distribution has important implications when considering the fate and bioavailability of metals recently introduced to the sediments. Because recently introduced trace metals are not necessarily distributed between sediment fractions in proportion to the size of each fraction, they may accumulate for long periods in fractions which are either highly available to deposit feeders or not at all. Their distribution will depend entirely on the kinetics of the exchange reactions involved. For example, based on the distribution of total zinc in this experiment we would expect that almost 45% of the added zinc-65 would be retained in the most available Fe/Mn oxide fraction. Instead, only 30% of the zinc-65 was acccumulated in this fraction. Recently added zinc is therefore less available to organisms then suggested by the chemical partitioning of zinc in these sediments.

Determination of the availability of a recently added metal will depend not only its absolute uptake by a bioavailable fraction, as controlled kinetically, but also on the size of the fraction. For a given uptake of trace metal, a bioavailable fraction already containing a large amount of this metal will experience a smaller proportional increase in this metal than that of another bioavailable fraction containing less of the metal. The smaller the proportional increase in a trace metal within a bioavailable fraction, the less significant the increase in exposure of the deposit feeder to the metal. It is of course possible that both the uptake kinetics and the size of the fraction are functionally related.

In this experiment measurements of the specific activity of zinc-65 in each chemical fraction combine both the absolute uptake of the label and the size of the each zinc fraction to express the fractional increase in zinc-65 in each fraction for a given addition of zinc-65 to the sediments. Consideration of both the specific activity of each fraction and its bioavailability, therefore, indicate the fate of small quantities of zinc added to the sediments. In general, for any metal-radionuclide system, the greater the specific activity in a bioavailable fraction, the greater the exposure of an organism to the trace metal. In Toronto Harbour sediments, the specific activity of zinc-65 in the bioavailable Fe/Mn fraction was low relative to the other fractions. Three other chemical fractions, (exchangeable, interstitial and carbonate bound) had higher specific activites and therefore exchanged much more freely with other fractions or soluble zinc. The effects of small additions of zinc to the system are therefore mitigated both by the slow rates of uptake of zinc by the Fe/Mn oxide fraction and the magnitude of the fraction itself.

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Application of the Fugacity/Activity Model to Predicting the Behaviour of Arsenic in Lakes

by

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Abstract

A family of general and conceptually simple models has been developed that is capable of predicting the behaviour and fate of contaminants. The models are based on thermodynamic principles with an equilibrium criterion replacing the use of concentration. Fugacity is the criterion used for organic chemicals that partition between air and water phases, and activity is used for inorganic chemicals with negligible vapour pressure.

The aim of the study described in this paper is to develop an activity-based mechanistic model for predicting the fate of inorganic contaminants in fresh waters. The model is being applied to arsenic in Moira Lake, located in eastern Ontario. This lake has had elevated arsenic loadings for over 100 years from an upstream, now-abandoned mine and mineral processing facility. The study is comprised of four components: a field study of Moira Lake, a study and subsequent modelling of arsenic dynamics between the water column and sediments in lake enclosures using a radioisotope of arsenic, laboratory studies of sediment-water exchange, and synthesis of all results into a comprehensive fate model for arsenic in Moira Lake.

The structure of the research program is described, and progress on the various components is reviewed.

Introduction

Many situations exist in which sediments have been contaminated as a result of previous industrial and municipal discharges or spills. In these "in-place" pollutant situations, the regulatory problem is often to determine the amounts of chemicals present, their bioavailability, the response or recovery time of the system, and whether artificial remediation is preferable to natural remediation. One approach to the problem is to assemble a mathematical model of the situation and use it to explore possible actions. Such models are obviously useful only if they are valid, that is, if they give a reasonably accurate description of reality. They should be based on equations which describe real physical, chemical, and biological processes. Perhaps the most successful models of this type in the aquatic environment have been the dissolved oxygen or reaeration models and the phosphorus models, which were used to predict the effect of reduced phosphorus loadings on the Great Lakes. Such models have been perceived to be very successful, although surprisingly little effort has gone into validating the phosphorus models. A recent IJC publication reviews the use of models in such situations (IJC, 1986).

To assist in providing a general and easily understood environmental model capable of predicting the fate of contaminants, our group has developed a family of models based on thermodynamic principles. The central concept is that concentrations are replaced by an equilibrium criterion, thus simplifying expressions for intermedia transport. For organic chemicals that partition between air and water phases, fugacity is the equilibrium criterion used. For inorganic contaminants that have a negligible vapour pressure, activity is preferable. Both fugacity and activity are linearly related to concentration, and models written in any of these terms are, ultimately, mathematically equivalent.

The objective of our research is to develop a mechanistic model based on activities to describe inorganic contaminant movement in fresh waters with emphasis on water-sediment exchange.

In this paper, we describe progress on a Ministry funded project, the goal of which is to assemble a reliable model which describes the past, present, and future behaviour of one contaminant (arsenic) in one lake system, Moira Lake, near Belleville. Moira River and Lake have received arsenic inputs for over 100 years from an upstream, now-abandoned mine and mineral processing facility at Deloro. In 1979, the Ministry initiated a site clean-up, and since then has been treating arsenic-rich leachates flowing into the Moira River. To date, total expenditures on this project has been in excess of $2.5 million and annual operating cost are about $250,000. Despite these efforts, some arsenic still enters the river at Deloro, and the contaminated sediments of Moira Lake provide a source of arsenic to the overlying water. To develop a comprehensive model of this system, our project has involved four related components that are outlined below.

1- A field study is being conducted to investigate the levels of arsenic and various limnologic parameters in the water, suspended sediments, and bottom sediments of the Moira Lake system at regular intervals over a full year, including winter conditions. We have been helped in this process by previous studies and by the assistance of the Ministry of the Environment, Southeastern Region. It is a pleasure to acknowledge their cooperation, particulary that of Glenn Owen.

The analyses of Moira Lake samples for total arsenic content are being done with the collaboration of Dr. S. Landsberger of the University of Illinois.

2- We have undertaken a study of the dynamics of arsenic as it migrates between the water column and bottom sediment of limnocorrals or small enclosures in a lake. This work was done in conjunction with Dr. R.J. Cornett of Atomic Energy of Canada Ltd. at Perch Lake, within the property of the Chalk River Nuclear Laboratory. The study was designed to improve our understanding and to build a simple model of arsenic dynamics within a lake by monitoring the movement of As-74, a radioisotope of arsenic, within the lake enclosures. With the use of As-74, we have been able to quantify and model its movement due to sediment deposition, resuspension, and diffusion, the major processes influencing the disappearance of arsenic from the water column and its subsequent reappearance from sediments.

3- In order to provide a detailed view and to quantify the process, a laboratory system has been developed for exploring the equilibria involved in the exchange of arsenic between sediments and water as a function of temperature, pH, and Eh. It is believed that this system may have utility beyond this study as a tool for investigating the availability of "in-place" pollutants, for example, their tendency to migrate back into the water column.

4- The final and most important step is the assembly or synthesis of the environmental information, the water column-sediment exchange studies, and the sediment equilibria findings into a comprehensive model of the behaviour of arsenic in the Moira Lake system over the period 1860 to the present, and extending to the future. In this report, we discuss the progress of these four component studies individually.

Field Study of Moira Lake

The Moira River system in eastern Ontario has experienced elevated arsenic loading since gold mining and arsenic, cobalt, and nickel processing activities began around the village of Deloro in 1866. Arsenic and heavy metals from this source have been removed from the river at the major sediment deposition zones of Bend Bay, Moira Lake, and Stoco Lake. So that we may model the system, it has been necessary for us to augment existing information concerning Moira Lake and to reconstruct historical arsenic loadings to the system using sediment records.

Moira Lake is a large (837 ha), shallow (mean depth 4.4 m) lake located approximately 50 km north of Lake Ontario at Belleville (44°30' N, 77°27' W). The lake is located at the contact zone between sedimentary limestones, and metamorphic and igneous bedrock. As a result of the lake's large catchment area (some of which is used for agriculture), its shallow depth and the weathering of underlying limestones, the pH, total dissolved solids content, hardness, and alkalinity of the lake are all high. Whereas it is classed as a single lake, a constriction separates the lake into two, functionally separate basins: a smaller basin to the west and a larger one to the east. In this study, these two basins are treated as separate units. For modelling purposes, we also include Bend Bay (which is located just upstream of Moira Lake) as a separate hydraulic segment, since it is believed to be a significant trap for sediments. Figure 1 is a map of the area.

Our field study has involved a one-time sampling of fish of the lake and periodic sampling of the water and sediments of Bend Bay and Moira Lake.

Fish from the two basins of Moira Lake were collected for analysis in 1986 in conjunction with the fish sampling program of the Ministry of Natural Resources (Tweed District). A total of 27 fish from six species were taken from trap nets set throughout the lake. The fish were weighed, measured, and if possible, sexed. Samples were taken of muscle, liver, and for some of the fish, skin. These samples are currently being analyzed for total arsenic content.

Based on an understanding of arsenic dynamics garnered from our enclosure experiments, we designed a program to sample the water and sediments of Moira Lake. For example, although our previous models accommodated dissolved and a single particulate fraction of chemical in the water, results from our enclosure work suggested that different particulate size fractions influence arsenic dynamics. Consequently, we designed our sampling regime to include four particulate size classes.

We have sampled the water and sediments of Moira Lake at monthly intervals from June to October. These trips involved collecting water just below the water surface at the inflow, outflow, and Bend Bay, and a depth-integrated water column sample from the surface to within 1 m of the sediments at the deepest location in the west and east basins. At these two stations and at Bend Bay, we also took zooplankton tows (110 um mesh), a temperature profile of the water column, Secchi disk depth, and we collected several sediment cores using a modified K-B corer. Finally, at the deep sampling sites and at a shallow site (4 m deep) within each of the west and east basins, we collected samples of sedimenting particulates using cylindrical sediment traps. Three traps with a height:diameter ratio of 6:1 were deployed at each of the four sites for 48 hours.

The water samples from the inflow, outflow, Bend Bay, and the two basins were separated into dissolved and three particulate fractions using 20 um mesh screens and pre-weighed 1.2 um and 0.45 um membrane filters within 24 hours of collection. Water overlying the sediments in the sediment core tubes was handled in the same way (this water oxic). Samples of unfiltered and filtered water were preserved with one percent Ultrex nitric acid and stored refrigerated in acid-washed plastic bottles.

Before filtering, subsamples were taken of particulates collected in the sediment traps, and the remaining particulates were collected on pre-weighed 1.2 um glass fiber filters. These filters, as well as the 1.2 um and 0.45 um membrane filters on which the water column particulate samples were collected, were weighed and then stored until analysis for their arsenic content. The subsamples of the sediment trap particulates were analyzed by means of a Coulter counter to determine the size distribution of sedimenting particles.

Two cores per basin and Bend Bay were sectioned at 2 cm intervals under a nitrogen atmosphere. As well under nitrogen, the pore water was separated from the solid sediments by centrifugation and subsequent filtering using 0.45 um membrane filters. These pore water samples were preserved with one percent Ultrex nitric acid. The solid sediments were transferred to vials, dried at 50°C for several days, and then weighed in preparation for analysis.

With the remaining sediment cores, we measured Eh and pH at 1 cm intervals down to 20 cm below the sediment/water interface. On one occasion, the water content and loss on ignition of sediments was determined for each 2 cm section of cores collected from the three sites.

All samples taken from Moira Lake, including waters, pore waters, particulates on filters from water samples and sediment traps, zooplankton, sediments, and fish tissue, are being analyzed for total arsenic by means of neutron activation analysis at the University of Illinois in a collaborative project with Dr. S. Landsberger.

Neutron activation analysis is an extremely sensitive method to determine arsenic in the environment, and numerous papers have appeared on this technique. However, for the determination of arsenic in water at concentrations of several nanograms per gram, a relatively high neutron flux is preferred so that good counting statistics can be achieved for reliable precision.

Typically, sediments (0.5-1.0 g) were irradiated at a flux of $1.5x10^{12}$ n $cm^{-2}s^{-1}$ for a period of 2 hours. A delay time of 5-7 days and a counting time of only several minutes was needed to achieve a precision of 1-3% and detection limits of 10-20 ug/g. These detection limits could easily be reduced, but this was not necessary since typical concentrations were between 400-1200 ug/g.

The particulate samples collected on filters were irradiated with a flux of $4.5x10^{12}$ n $cm^{-2}s^{-1}$ for a period of 3 hours. Depending on the type of filter and its matrix, detection limits varied from 0.01-0.8 ug with a precision of 2-3%. Decay times were from 3-7 days with counting periods from 10-15 minutes.

The determination of water and pore waters was found to be optimized using a 3 hour irradiation at a flux of $4.5x10^{12}$ n $cm^{-2}s^{-1}$, a delay time of 15-24 hours, and a counting time of 10 minutes. Typical precision was 15% and a detection limit of 1-5 ng/g.

Calibration was done using standards from atomic absorption solutions and checked with the analysis certified reference materials. Radioactive counting was done using a state-of-the-art high resolution counter with an efficiency of 19%.

Preliminary Results

It is evident from our preliminary results that arsenic levels, as well as many limnologic conditions, vary considerably with lake segment and time of year. Bend Bay is a very shallow (1 m deep) enlargement of the Moira River. Water transparency is extremely low (1.2-2.0 m Secchi depth, depending on the month), and a substantial portion of the suspended particulates consists of fine particulates. The surface sediments, which are 98% pore water, contain 0.7 to 0.8 ppm total arsenic or about 0.1% of the arsenic concentration in the solid sediments. This ratio of arsenic in the pore water to sediments decreases with increasing depth into the sediments. The concentration of arsenic in the solid sediments reaches a maximum at 6 to 14 cm below the sediment/water interface. Negative Eh values rise in the sediments from 2 cm below the interface in spring and early summer to 1 cm below in late summer.

The west basin of Moira Lake is about 300 hectares in area, with a uniform depth of 3 m (excluding two holes extending to 8 m depth). Secchi depth readings vary from 4 m in spring to 1 m in summer, when productivity is highest and thermal stratification may occur. The sediments, which are similar in consistency but have a 5% higher organic matter content than that of Bend Bay, appear to be anoxic year-round at depths greater than 1 cm below the sediment/water interface. However, the actual Eh potential of these sediments and the immediately overlying water varies from maximal values in spring to minimal values in mid-summer. Arsenic in the pore waters of these sediments follows the pattern observed in the Bend Bay sediments; values are highest at the surface and decrease with increasing depth. Arsenic in the solid sediments reaches a peak concentration of over 1000 ppm at 8 to 12 cm below the sediment/water interface.

The east basin of Moira Lake is the largest of the segments we are modelling. It has a surface area of about 500 hectares and three deep areas within the generally shallow basin. Secchi disk readings are similar to that of the west basin. But, unlike the west basin, limited thermal stratification develops in the east basin because of its long fetch and shallow depth. The summer-long bloom of filamentous blue-green algae suggests that the east basin is the most eutrophic and productive of the three segments we are modelling. Because of this productivity, the concentration of suspended particulates was highest in this segment, despite the fact that much of the inflowing, heavy inorganic particles sediment in Bend Bay and the west basin. Another consequence of this productivity is the extremely loose and floccy consistency of the sediments. The surface layer of sediments contains only 0.04% solids, of which 45% is organic matter. Of the three segments, the sediments in the east basin appear to have the highest Eh levels, which may be attributable to their extremely loose and floccy consistency, their high water content, and the long, shallow basin morphometry that enhances water circulation. Anoxia prevails in these sediments at 3 to 4 cm below the sediment/water interface in fall and spring but rises to 1 cm depth in mid-summer.

Contrary to the pattern observed in Bend Bay and the west basin, the concentration of arsenic in the pore water of the east basin increases with increasing depth into the sediments and is very low (0.04 to 0.05 ppm) at the surface. In the solid sediments, a peak in arsenic concentration is found 8 to 12 cm below the interface, as in Bend Bay and the west basin, but interestingly, a second peak was observed at the surface in spring and fall. This surface peak of over 1000 ppm was not found during summer.

The levels of arsenic in the lake water also vary among segments and seasonally. In spring, the levels in Bend Bay are about 0.06 ppm, 80% of which is dissolved. Travelling downstream, the levels in the west basin fall to 0.03 to 0.05 ppm and in the east basin and outflow they are lowest at 0.02 to 0.03 ppm. However, in fall 1986 the reverse trend was observed, with arsenic levels of 0.025 ppm in the inflow and west basin and 0.055 ppm in the east basin and outflow.

These data, in addition to a crude mass balance of the river system from just below Deloro, where the arsenic enters the Moira River, to Moira Lake itself, suggest that in certain seasons, such as winter and spring, the arsenic levels within the lake exceed that entering. The magnitude of this "negative retention" appears to be increasing from year to year and duration within the year.

The results briefly outlined above, together with those forthcoming from the arsenic analysis of additional samples, are being used to build a model for Moira Lake. The model will be adapted to accommodate seasonal changes in the temperature regime and redox potential in the lake and sediments.

The Study of Sediment-Water Exchange Dynamics in Lake Enclosures

As mentioned in the introduction, in order to understand the factors affecting arsenic movement within a lake, and to build and test a simple model to describe this movement, we conducted experiments involving the addition of radioisotopes to enclosures in a lake. This experiment was done in conjunction with Dr. R.J. Cornett of the Atomic Energy of Canada's Limited's Chalk River Nuclear Laboratory at Chalk River, Ontario.

The enclosures were installed in Perch Lake, a small (45 ha area), shallow (mean depth 2 m), soft water lake located on the Canadian Shield in the Ottawa River Valley (77°22'W, 46°2'N). The lake is dimitic (circulates twice a year), does not stratify, and is dystrophic or a bog lake high in organic material.

A total of 8 enclosures were installed in Perch Lake on June 4, 1986. The enclosures were 0.8 m in diameter, approximately 2 m deep, and open to the sediments. The bags were made of heavy gauge plastic and were held open by hollow rings of PVC tubing: a top ring that was fixed to floating rafts at the lake surface, a middle ring 1 m below the surface of the water, and a weighted bottom ring that sank 10-15 cm into the sediments. The design of the bags is discussed more fully by Chant and Cornett (1987).

Fifteen isotopes were added to 6 of the enclosures, and 9 of these were added to the remaining two enclosures. Most of the isotopes were carrier free and in a chloride salt form. The specific activities were high enough so that the concentrations of the elements in the enclosures were not significantly increased. Of the eight enclosures, two were monitored as controls, two (with the 9 isotopes) contained fish, while the remaining four were manipulated with addition of particulates and humic substances. In this paper, we will discuss the results from the four former enclosures.

To monitor the flux of particulates and radioisotopes to the sediments, sediment traps with a height to diameter ratio of 5:1 (Bloesch and Burns, 1980) were suspended 1 m above the sediments in each bag and in the lake. Adsorption of isotopes to the bag wall was monitored by counting the activity on plastic strips hung in one of the control bags.

Following the addition of isotopes to the bags, samples of water, suspended particulates (>0.4um), sediment trap material, and plastic strips were sampled every other day for 21 days. After 21 days, the walls of 2 of the bags were slit, the overlying water thoroughly flushed for 3 days, and new bags were placed in the same position as the old. The release of isotopes from the sediments was then monitored by measuring activity in the overlying water. This was done every few days with decreasing frequency with time for a further 50 days.

All samples were analyzed for activity by gamma spectroscopy. The sample counts were corrected for detector efficiencies, geometry effects, and radioactive decay, and calibrated using standard sources prepared by A.E.C.L. All results have been expressed relative to the day the isotopes were added to the enclosures. Potential artifacts due to the enclosures were found to negligible (Chant and Cornett, 1987). Further details of the enclosure design and methods used in this study has been presented by Chant and Cornett (1987).

Summary of Results

During the first two weeks of the experiment, the losses of arsenic from the water (as well as the other isotopes added) was log-linear and was well described by the model. After two weeks, when wall effects became pronounced, the loss rates diminished and the model's predictions were biased (Figure 2). The initial loss rates were comparable to those reported by Hesslein et al. (1980) and Schindler et al. (1980) for radioisotopes added to large lake enclosures at ELA. For the second portion of the experiment, the model effectively predicted the reappearance of arsenic into the water column as a result of desorption from the sediments (Figure 3). Observed and predicted behaviours of the tracers were more similar than we expected a priori.

The fit of the model to a single tracer's experimental behaviour is not particularly noteworthy. However, it is significant that we obtained agreement between predicted and observed values for different enclosures by changing only the measured sedimentation rate and concentration of suspended particles, and for a wide variety of tracers (ie., Zn, Hg, Fe, and Sn) in which the only metal-specific variable was K_D (Figures 4 & 5). This agreement raises two points. First, this simple model can predict the behaviour of metals that varied from 13% (Zn) to 30% (As and Hg) to 80% (Sn) particle-bound, although there are discrepancies between predicted and observed desorption values for some tracers. Second, the results show that the factors controlling the rates of transport of particle-bound and dissolved species are similar (Diamond et al. 1987).

A sensitivity analysis of the model clarified these two points. The model is most sensitive to changes in sedimentation/resuspension and diffusion rates, and the depth of the layer of "active" sediments. This layer represents the depth from which tracers in the sediment can return to the water column during the time of the experiment. We estimated this depth at 6 mm by fitting the model to the experimental observations. We also found that the magnitude of tracer movement by diffusion is comparable to that by particle sedimentation, the exact values being controlled by a tracer's K_D. For arsenic, 60% of the tracer moved by diffusion and 40% was due to sediment deposition processes. In contrast, 13 and 87% of the tin tracer moved by diffusion and sedimentation, respectively.

Comparing the results obtained from enclosures differing in suspended particle composition, we found that, in addition to the above-mentioned factors, the types of suspended particles in the water column strongly influenced tracer movement. For example, humic acids added to the water column decreased the rate of tracer loss by suspending them in the water, whereas added inorganic particles increased the rate of tracer loss by increasing the sedimentation rate.

Using this information, we have gained an understanding of the importance of the various transfer processes affecting arsenic dynamics in a lake. This understanding has helped us in our field studies of Moira Lake. It has also facilitated application of the simple model developed for lake enclosures to a more sophisticated model for the Moira Lake system.

Laboratory Studies of Sediment-Water Exchange

It is clear that in Moira Lake and other similar situations, the prevailing water quality is being controlled by the exchange of contaminants with the sediments. Assessing these situations, some key questions arise, such as:

(i) What are the relative amounts of the contaminant in the water column and sediment (as controlled by equilibrium)?
(ii) How fast does the contaminant migrate from sediment to water?
(iii) For how long will the contaminant continue to "bleed" from sediments, given that they may become depleted or buried?
(iv) What roles do temperature, pH, and Eh play in modifying these dynamics?

A key contribution to this area has been the concept of the sequential extraction of elements from sediments developed by Tessier and others at INRS, Quebec (ie., Tessier et al. 1979). We have exploited and modified this concept to develop a system in which a volume of contaminated sediment is gently mixed with water and subjected to a continuous through-flow of water at a controlled rate, temperature, pH, and Eh. The aqueous extraction of the contaminant from sediment is followed by analysis of the exit water for changes in contaminant concentration. A sketch of the system is given in Figure 6.

The data from such an experiment are presented in the form of a plot of fraction of contaminant remaining as a function of laboratory time or volume of water passed through the system, as shown illustratively in Figure 6. From the model, we believe that it is possible to define an equivalent volumetric rate at which lake water is exposed to a given volume of sediment in a natural situation. This exposure is due to pore water diffusion and sedimentation/resuspension. Given the volumetric rate of water to sediment exposure, we can then calculate the lake time which is equivalent to the laboratory time. For example, a mass of sediment may be exposed in the laboratory in one day to contact with 10 litres of water. In the lake, diffusion dictates that the same sediment mass is effectively exposed to 0.1 litres of water, the lower volume being due to the sluggish diffusional regime. Alternately, in the laboratory, it is possible in 3 or 4 days to simulate the exposure of the lake sediment to water for 1 year. We can thus use the laboratory system to "accelerate time" and probe the likely future behaviour of sediments, ie., how fast they will be depleted of contaminant.

Particularly important in this experimental situation is the facility to alter exposure conditions and to examine how changes in pH, temperature, or Eh will affect the mobility of the contaminant. In terms of Moira Lake, we suspect that redox potential plays an important role in controlling arsenic mobility.

We have conducted several experiments with this apparatus using sediments and water from Bend Bay and the west and east basins of Moira Lake. In the experiments, we have manipulated Eh conditions to simulate the passage of well aerated water through oxic sediments and water with minimal oxygen through anoxic sediments. The water samples from these experiments are now being analysed for their arsenic content by means of graphite furnace atomic absorption spectrophotometry.

We are optimistic that the technique will prove to be valuable for elucidating the behaviour of arsenic in Moira Lake and of other organic and inorganic contaminants which cause an "in-place" pollutant problem.

Model Development

It is too early to provide meaningful results for the model, but it is of interest to describe its general structure and the expected results. Figure 7 shows the important processes and segmentation of hydrologic units.

The model is segmented into Bend Bay, West Basin of Moira Lake, and East Basin of Moira Lake. Water flows into Bend Bay are defined from hydraulic records taken upstream by Environment Canada on a monthly basis.

Because of the widely differing physical, chemical, and seasonal characteristics of matter suspended in the water column, characteristics that affect arsenic movement, we recognize four size classes of particulates in the model. The classes are functionally defined by mesh and filter sizes: >110 um, 110-20 um, 20-1.2 um, and 1.2-0.45 um. These classes correspond to zooplankton, net phytoplankton and particles >100 mesh, nanoplankton and particles <400 mesh, ultraplankton, and finally bacteria, viruses, and large colloids. Arsenic found in the water that passes the 0.45 um filter is considered dissolved.

A mass balance for each type of suspended sediment is defined for each segment on a monthly basis and includes terms for sedimentation, formation, degradation, inflow, and outflow. Rates of diffusion for dissolved arsenic are also defined.

Because of sediment focussing processes, we consider diffusion and sediment resuspension to occur from sediments where the water column depth is greater than the mean depth of the segment. At present, this "active" layer of sediment is treated as being of fixed depth, but it is envisaged that a model including vertically layered sediment will be developed. In this model, there will be the capability of modifying sediment redox conditions and thus sediment pore water equilibria.

The model calculations involve numerical integration of two differential equations (for water and sediments) with periodic printout of prevailing conditions. In many respects, the approach taken is similar to that of the QWASI lake models for organic contaminants (Mackay et al., 1983) in which fugacity, rather than activity, is the dominant variable. It is intended that the model be run to treat the period 1850 to 1987 and to predict future trends in water and sediment quality.

Conclusions

An experimental program, involving field and laboratory studies, and a modelling effort have been described in which the general aims are:

(i) to improve our understanding of the dynamics of arsenic in fresh water lakes in general, and Moira Lake in particular, and

(ii) to provide a successful specimen or "case study" in which environmental and laboratory data are synthesized in the form of a model to provide the Ministry with a clearer picture of the severity of the present conditions, the likely magnitude of changes in the future, and the benefits and costs of remediation.

It is envisaged that the project will be completed in mid-1988.

Acknowledgements

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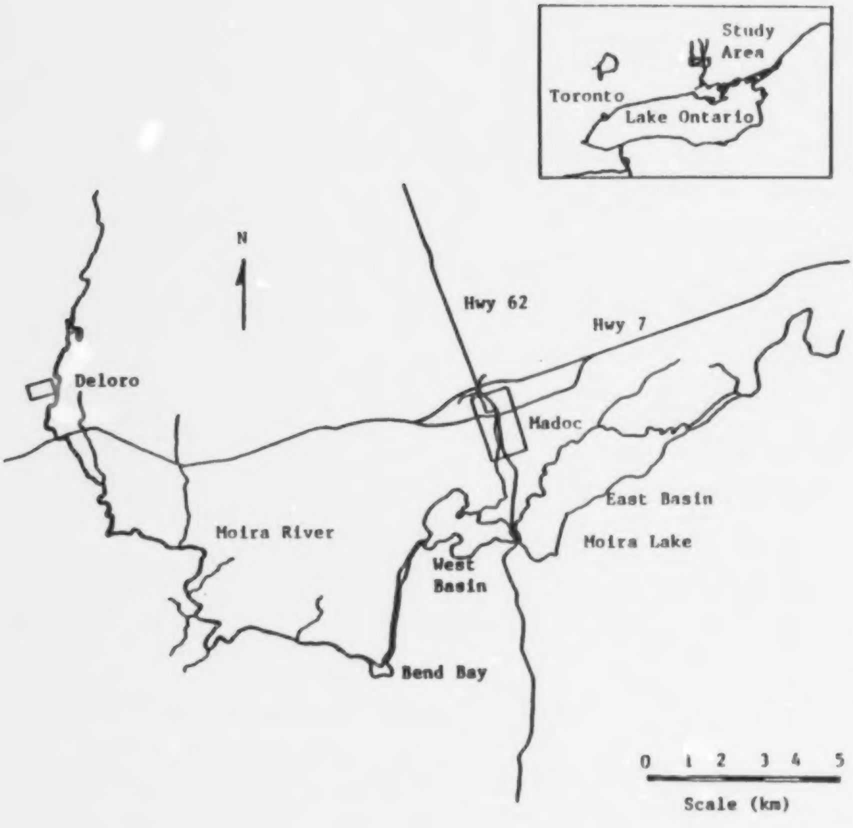
Study
Area
Toronto
Lake Ontario
N
Hwy 62
Hwy 7
Deloro
Madoc
East Basin
Moira Lake
Moira River
West
Basin
Bend Bay
0 1 2 3 4 5
Scale (km)

Figure 1. Location of study area.

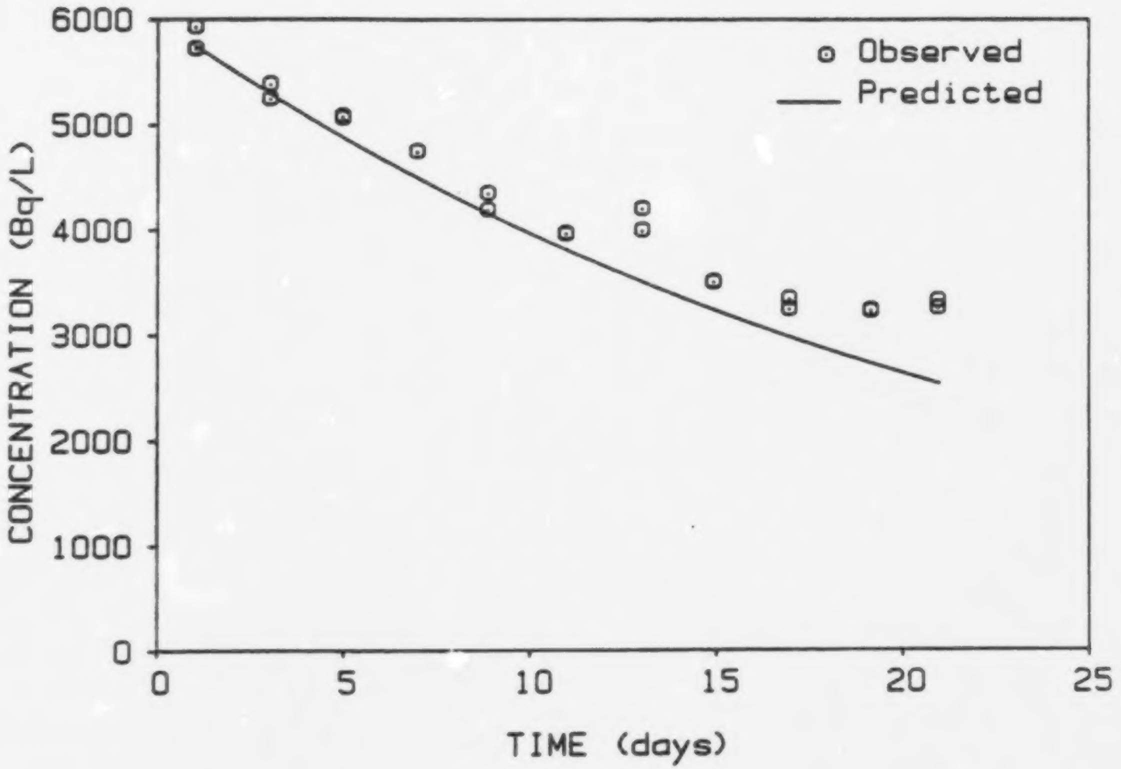

Figure 2. Observed and predicted loss of arsenic (as As-74) from the water column in lake enclosures.

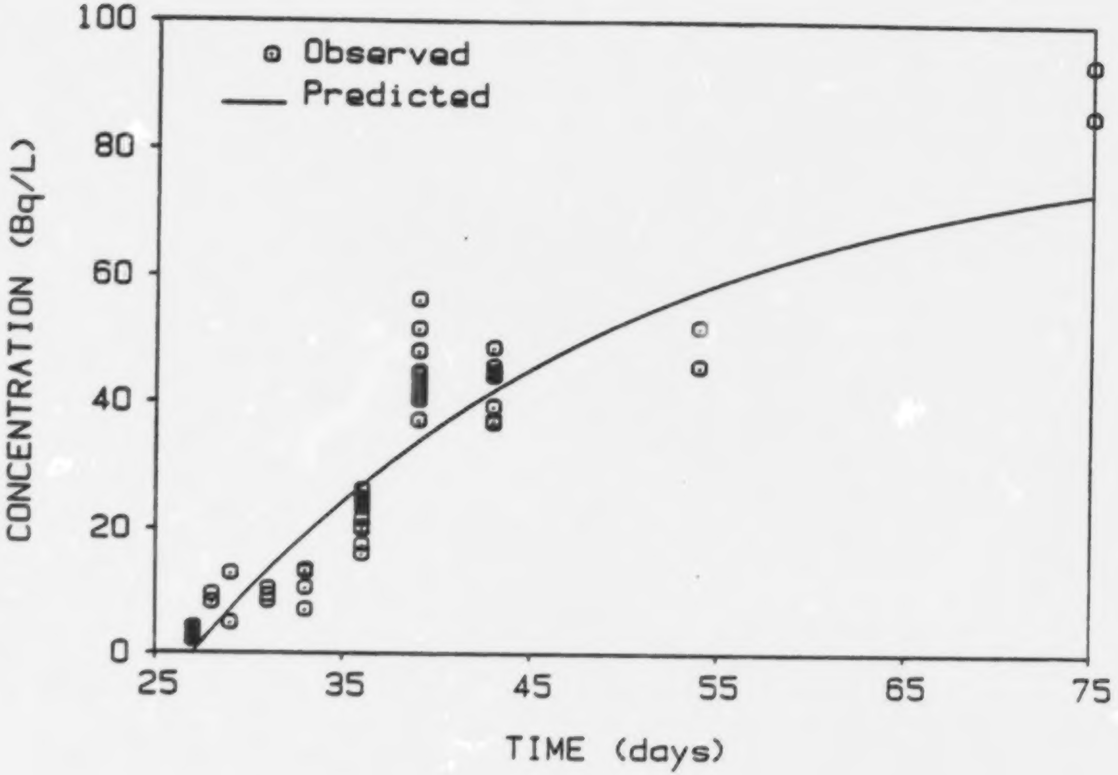

Figure 3. Observed and predicted desorption of arsenic (as As-74) from sediments into the water column in lake enclosures.

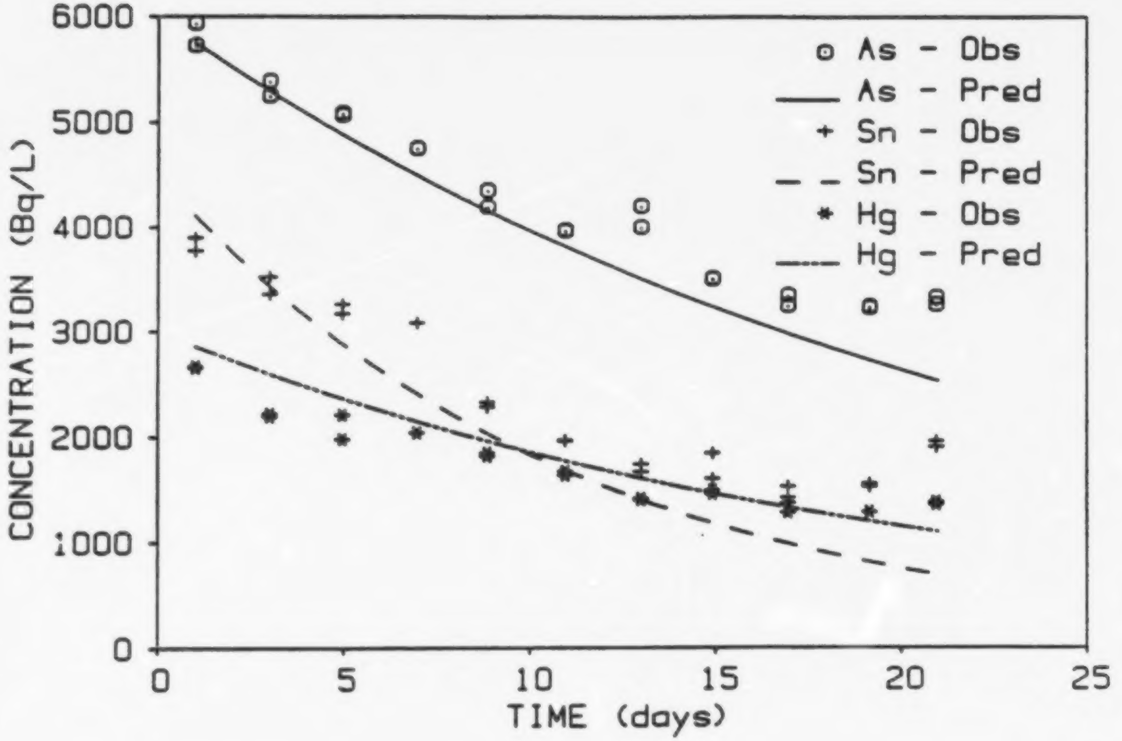

Figure 4. Observed and predicted loss of arsenic (As-74), tin (Sn-113) and mercury (Hg-203) from the water column in lake enclosures.

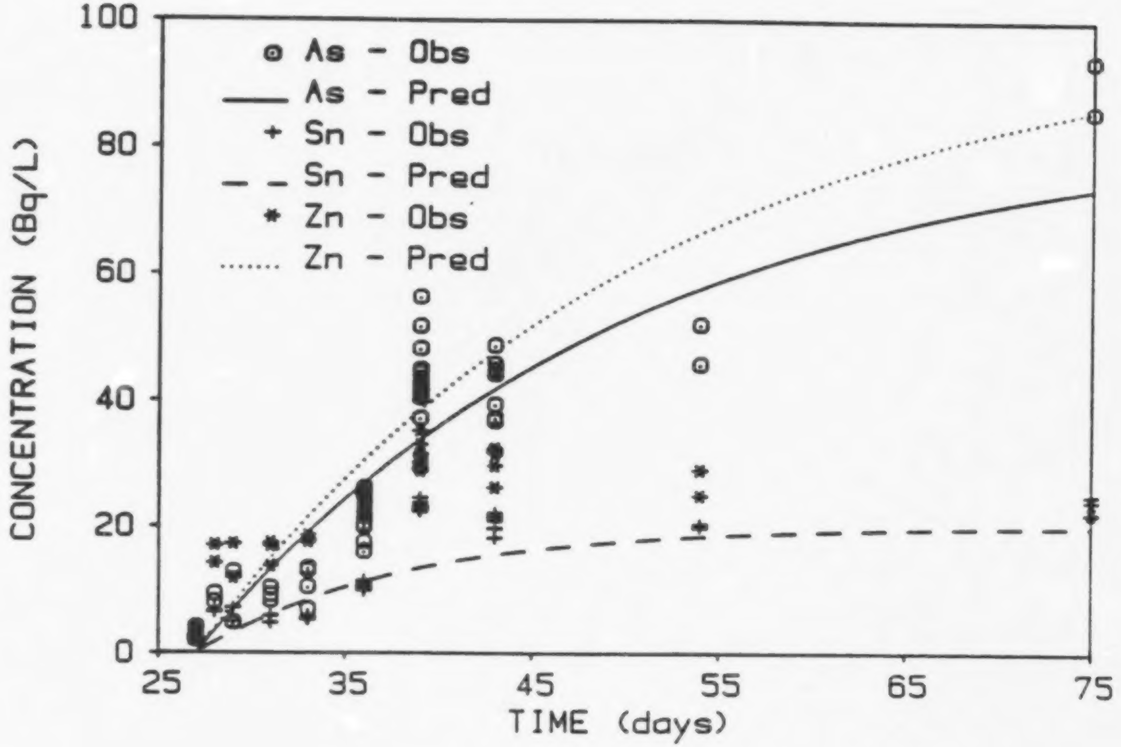

Figure 5. Observed and predicted desorption of arsenic (As-74), tin (Sn-113) and zinc (Zn-65) from sediments into the water column in lake enclosures.

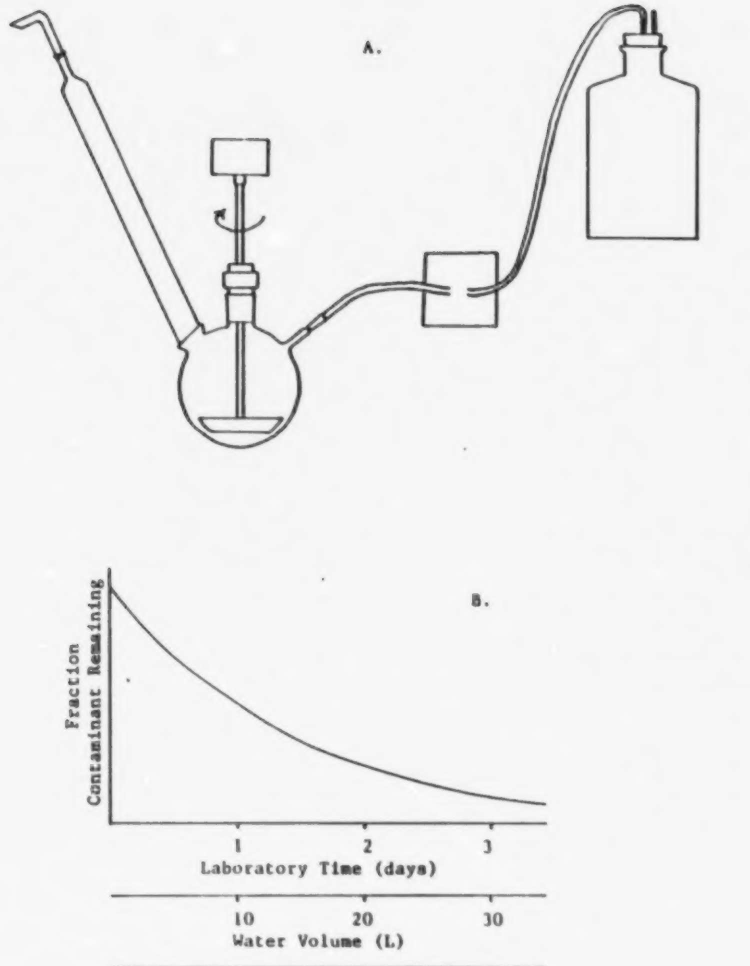
A.
B.
Fraction Contaminant Remaining
1
2
3
Laboratory Time (days)
10
20
30
Water Volume (L)
100
200
300
Lake Time (days)

Figure 6. Illustration of the method used to study sediment-water exchange of arsenic by aqueous extraction. A. Flow-through system used to contact sediment with water under controlled conditions, B. Depiction of results obtained from aqueous extraction experiment in which time and water volume used in the laboratory are related to that in the lake.

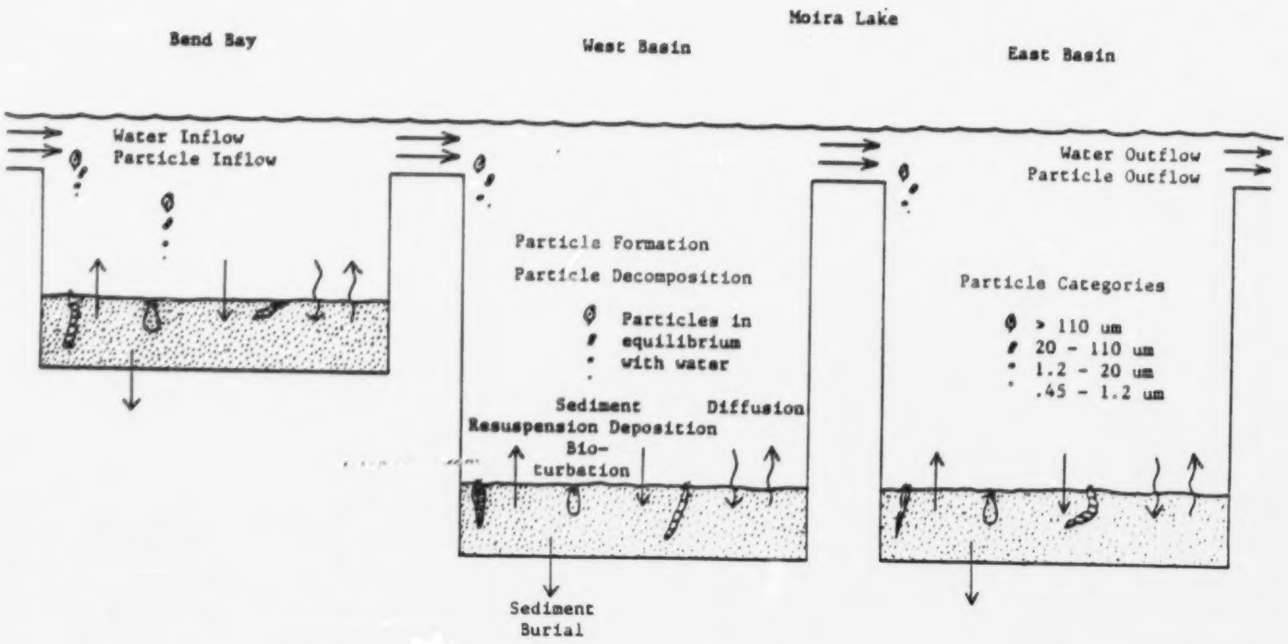
Moira Lake
Bend Bay
West Basin
East Basin
Water Inflow
Particle Inflow
Particle Formation
Particle Decomposition
Particles in equilibrium with water
Sediment Resuspension
Deposition
Bio-turbation
Diffusion
Sediment Burial
Particle Categories
> 110 um
20 - 110 um
1.2 - 20 um
.45 - 1.2 um
Water Outflow
Particle Outflow

Figure 7. Segmentation of hydrologic units and processes used to model the movement of arsenic in Moira Lake.

Degradation of Halogenated Benzoates by Anaerobic Bacteria in Lake Ontario Sediments

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ABSTRACT

Anaerobic bacteria from sediments collected at different sites in Lake Ontario were cultivated in the presence of halogenated benzoates. Biodegradation was assessed by net gas production (CH_4, CO_2), measured by pressure transducer and gas chromatography, and by substrate disappearance using high pressure liquid chromatography (HPLC).

When sediment from each site was suspended in revised anaerobic mineral medium (RAMM) and enriched in the presence of halogenated benzoates, Toronto Harbour slurry was characterized by high metabolic activity, as monitored by gas production and rapid substrate depletion, in comparison to Humber Bay slurry. A characteristic metabolic pattern was exhibited with preference for 3-bromobenzoate (3-BrBZ) and 3-iodobenzoate (3-IBZ) to 3-chlorobenzoate (3-ClBZ). Degradation in basic (not enriched) sediments showed a prolonged lag phase (6 - 10 weeks) in comparison to enriched sediments (2 days), suggesting a possible acclimation process. HPLC analyses detected a transient accumulation of benzoic acid in the cultures during biodegradation, indicating a reductive dehalogenation pathway.

Bacteria grown on agar roll tubes were characterized by the Gram stain and by phase contrast microscopy as highly diverse. The community consisted of Gram negative and positive cocci, Gram negative rods, and spiral forms. The organisms seemed to operate as a consortium.

The results suggest that there exists a potential for anaerobic mineralization of halogenated contaminants in Lake Ontario and other freshwater ecosystems. Thus, once the consortium is identified, and its metabolic activities known, this approach could be applied in the industrial sector to the degradation of wastes under controlled conditions prior to their release into the environment.

INTRODUCTION

Xenobiotics, synthetic organic compounds and potential carcinogens and teratogens, are currently being discharged into the Great Lakes with industrial waste and farmland runoff. These contaminants, such as halogenated aromatic pesticides and polychlorinated biphenyls (PCB's) adsorb to particulates in lake water and settle in the sediment where they persist and may biomagnify up the food chain, thus endangering the health of humans and other animals. Many of these compounds were originally believed to be recalcitrant. Within the past three years, several research groups have found that chlorinated benzoates, breakdown products of PCB's and some herbicide congeners, as well as chlorinated phenols, includinng wood preservatives, are decomposed in anaerobic test systems (Tiedje et al., 1986). During bacterial transformation, Cl atoms are removed from the aromatic ring; the dechlorinated products thus formed are less hazardous and more susceptible to further degradation by both aerobic and anaerobic microorganisms.

In the light of these findings, the biodegradative potentials of anaerobic bacteria from th sediments collected at two sites (Humber Bay and Toronto Harbour) in Lake Onario were assessed. Enrichment of the sediment culture with monohalogenated benzoates was applied in order to acclimate the organisms to the sequential biodegradation of polyhalogenated benzoates. A most recent addition to this project deals with the evaluation of biodegradation potential at six different sites in Lake Ontario.

Methods for measuring the biodegradative ability of sediment anaerobes (monitoring substrate depletion and measuring gas production) were developed. Morphological characterization of these microorganisms was included in this study.

METHODS

Sediment collection

Sediment samples were collected in Lake Ontario at Humber Bay (MOE station #335, depth 15m, Fig. 1) and inner Toronto Harbour (MOE station #1335, depth 8.5m, Fig. 2), and at sites listed in Table 1, (Figures 1-4),by Ponar sampler,and transferred to Mason jars filled to maximum capacity. The jars were tightly capped, and stored at 4°C in the dark until further use. .

Preparation of test medium

The revised anaerobic mineral medium (RAMM) used in this study was that described by Shelton and Tiedje (1984a);it contained various vitamins, minerals, redox indicator, buffer, and a reducing agent. Hungate technique and apparatus were used to sparge with 10% CO_2 - 90% N_2 gas mixture which was passed through copper fillings at 300°C to remove traces of oxygen. All methods for anaerobic gassing of bottles and for preparation of oxygen-free gases were essentially those of Hungate (Hungate, 1968).

"Feeding experiments"

October 1986 Sampling (Table 1)

Five hundred ml of the collected sediment transferred to 2-L Erlenmeyer flasks was suspended in RAMM in a 1:1 ratio. The flasks were sealed with thick butyl rubber stoppers. The stoppers were secured in place with tape and equipped with a needle attached to Nalgene tubing trapped in a test tube filled with water to maintain atmospheric pressure in the head space of the flasks. The substrates 3-ClBZ, 3-BrBZ, and 3-IBZ were added to the sediment slurry in the flasks at a 100 ugC/ml (100 micrograms of carbon in substrate per milliliter of total volume). This concentration was determined in preliminary experiments as the most suitable one. Incubation was carried out in the dark at room temperature. Substrate disappearance was monitored by HPLC; samples for HPLC analysis were withdrawn at regular time intervals, passed through a Millipore 0.45 um disposable filter and stored at $-10^{\circ}C$ until analysis. Once total substrate depletion occurred, as shown by HPLC, 500 ml of the slurry was suspended in fresh RAMM and enriched with 100 ugC/ml of the same substrate. Strict anaerobic techniques were adhered to during the experiment.

July 1987 sampling (Table 1)

The sediment from each site was suspended in RAMM as described above. The substrates 3-ClBZ and 3-BrBZ were tested at 100 ugC/ml concentrations with sediment from each of the six sites. In this study 3-IBZ was not included. Substrate disappearance was monitored by HPLC.

Cross - Acclimation Experiments

To flasks containing repeatedly enriched sediment already acclimated to a monohalogenated substrate, as confirmed by HPLC, were added 100 ugC/ml of a polyhalogenated substrate, 3,5-dichlorobenzoic acid (3,5-diClBZ) or 4-amino-3,5-dichlorobenzoic acid (4-NH_2-3,5-diClBZ). The progress of substrate disappearance was followed by HPLC.

Preparation of test bottles for total gas production measurement

Slurry was prepared using anaerobic techniques as described above. Wheaton serum bottles (160 ml capacity) were filled with 50 ml of RAMM and 50 ml of sediment slurry. After 24 hours the pressure inside each bottle was equilibrated to atmospheric pressure by means of venting with a needle. The following test compounds were added at 25ug C/ml, 50 ug C/ml, 100 ug C/ml and 200 ug C/ml: 3-BrBZ, 3-ClBZ, 3-IBZ, benzoic acid (BZA), phenol, cresol, 3,5-diClBZ, 4H_2-3,5-diClBZ and ethanol (positive control). Autoclaved (30 minutes, 10 lbs./sq. in.) and non-autoclaved control bottles containing 50 ml of slurry and 50 ml of RAMM were also included. The bottles were incubated stationary in the dark. All compounds were tested in duplicate.

Preparation of substrates

Water insoluble test compounds were first dissolved in 1N NaOH. Appropriate amounts of test compounds were dispensed through a disposable membrane filter (Millipore, 0.22 um porosity).

Measurement of gas production

Total gas by pressure transducer

Total gas production (CH_4 and CO_2) was measured by a pressure transducer equipped with a Hamilton valve and a P-8 adapter. Bottles were vented to atmospheric pressure after each measurement in order to avoid cumulative gas pressures beyond the response range of the P-8 adapter capable of measuring up to 50 ml of gas pressure. The pressure transducer was connected to a digital multimeter and powered by a 12 Volt solid state regulated power supply. The multimeter response (in milliohms) was related to milliliters of gas by means of a standard curve constructed by adding known quantities of CO_2-N_2 gas to a serum bottle containing 100 ml of RAMM. Net gas production was calculated by subtracting gas produced in unautoclaved control bottles from that produced in test bottles.

Methane by gas chromatography

Methane production was confirmed by injecting 5 uL of headspace gas from serum bottles into a gas chromatograph equipped with a flame ionization detector. The gas chromatograph (Varian 3700) was calibrated with known amounts of CH_4 gas. An equation for the standard curve was derived by linear regression analysis and the coefficient of correlation for the curve was calculated. Amount of methane gas was quantified by means of the standard curve equation and degradation was expressed as percentage of theoretical methane production based on the stoichiometry of degradation.

Calculations

The total gas produced was divided between CO_2 and CH_4 based on the stoichiometry of the reaction which can be calculated by the Buswell equation (Tarvin and Buswell, 1934):

$$C_nH_aO_b + [n - \frac{a}{4} - \frac{b}{2}]H_2O \dashrightarrow [\frac{n}{2} - \frac{a}{8} + \frac{b}{4}]CO_2 + [\frac{n}{2} + \frac{a}{8} - \frac{b}{4}]CH_4$$

Theoretical gas production was calculated as follows: Initial substrate concentration (100 ugC/ml) was 1.2 mmol. For 3-IBZ, 3-ClBZ, 3-BrBZ, n=7, a=5, b=2 ==> molar fraction of CO_2 = 3.375, of CH_4 = 3.625. Starting out with 1.2 mmol substrate concentration, the molar fraction of CO_2 = 4.05 mM, of CH_4 = 4.35 mM. Correcting for solubility (Shelton and Tiedje, 1984a), we obtain molar fraction of CO_2 = 1.42 mM (4.05 x .35), of CH_4 = 4.13 mM (4.35 x .95). Theoretical CO_2 production = 31.8 ml (1.42 mM x 22.4 l/mol); theoretical CH_4 production = 92.5 ml (4.13 mM x 22.4 l/mol). Theoretical percentage of CH_4 compared to theoretical total volume was calculated as 74.4%, and similarly, for CO_2, the percentage was calculated as 25.5%.

High pressure liquid chromatography

Samples for HPLC analysis were taken from flasks at regular time intervals, passed through a 0.45 Millipore disposable membrane filter, and stored at -10° C until analysis. Substrate depletion was monitored by high pressure liquid chromatography (Waters Millipore system, Waters 501 HPLC pump, Novapak C_{18} column, 50% methanol/1% acetic acid , UV absorbance at 254 nm, 5 uL of sample injected into injection valve). The retention times of significant peaks were compared with substrate standards (dissolved in RAMM). The area under the peaks was then related to the natural logarithm of concentration of substrate standards.

Roll tubes

Autoclaved (10 minutes, 10 lbs./sq. in.) roll tubes (RAMM + 3% agar), with a halogenated compound (3-BrBZ, 3-ClBZ, or 3-IBZ) incorporated at a 100 ugC/ml, were prepared using a Bellco tube spinner, and inoculated with 0.5ml of ten-fold dilutions of slurry obtained from enrichment flasks. Strict anaerobic technique was adhered to as in the case of preparing liquid media. Inoculated tubes were incubated in the dark at room temperature or in a 37°C incubator (Hoeniger, personal communication; Hungate, 1969).

Microscopy

Colonies growing in roll tubes were picked with a sterile Pasteur pipette, suspended in a drop of sterile water, and Gram stained. The agar drop technique (Hoeniger and Headley, 1969) was used for the preparation of slides for phase contrast-microscopy.

RESULTS

Gas production.

No significant amounts of gas were produced by the sediment organisms collected in Humber Bay. In fact, all test compounds showed lower amounts of gas produced than unautoclaved control bottles (Table 2, Fig. 5). On the other hand, positive control bottles (containing ethanol) showed significant gas production but only at substrate concentrations >50 ug C/ml (Table 2). Sediment organisms collected at the Toronto Harbour site showed positive gas production for all substrates tested (Table 2, Fig. 6).

Gas chromatography.

Calibration with different volumes of CH_4 (in headspace of serum bottles containing 100 ml of RAMM) gave the following results: 50ml, 14.6(peak height); 30 ml, 8.6(peak height); 0ml, 0(no peak). Using linear regression analysis, the best fitting line for these points was found to be $y = 1.172x - 2.3$, where y represents the peak height and x is the volume of methane gas (in ml). The coefficient of correlation for this line was determined to be 0.9997, which indicates a very close linear fit. Using the above equation, it was possible to determine the volume of CH_4 in test bottles once the peak height was known. In general, it was confirmed that CH_4 gas formed a certain fraction of the total gas produced in the test bottles. Amount of CH_4 (in ml) as determined by gas chromatography, and production of CH_4 expressed as percentage of theoretical CH_4 production (determined from the Buswell equation) are related in Table 3.

High pressure liquid chromatography

October 1986 sampling

Analysis of HPLC samples from Toronto Harbour and Humber Bay sites, both basic and enriched cultures, revealed substrate disappearance patterns as shown in Table 4. HPLC results further indicated a relationship between test compound disappearance and level of benzoic acid (Figures 7 to 10). In general, as a substrate was degraded,the concentration of benzoic acid first increased and then decreased as the substrate became depleted. HPLC also showed the presence of small amounts of accumulating intermediates, other than benzoic acid.

July 1987 sampling
Preliminary results

After 8 weeks of incubation in the presence of 3-ClBZ, substrate depletion did not occur for any of the sites. However, sediment collected at 3 of the sites, Ashbridges Bay, Humber Bay (MOE#1355), and Toronto Harbour (MOE#1375), showed partial substrate depletion after 3 weeks of incubation in the presence of 3-BrBZ. More data will be available at a later date.

Cross - Acclimation Experiment
Preliminary Results

Organisms enriched from Humber Bay sediment, and acclimated to 3-BrBZ after several successive additions of 3-BrBZ, were able to completely degrade the substrate. These organisms then were able to completely deplete 100 ug C/ml of 3,5-diClBZ within 3 days. Organisms enriched from Toronto Harbour sediment and acclimated to 3-ClBZ exhibited a faster rate of 3,5-diClBZ depletion than those from Humber Bay sediment. More data will be available at a later date.

Growth on Roll tubes

Tubes incubated at 37°C exhibited growth (transparent colonies, approximately 0.1mm in diameter) after 2 days for all three substrates (3-IBZ, 3-ClBZ, 3-BrBZ). Tubes incubated at room temperature showed growth (transparent colonies, approximately 0.1mm in diameter) after three to six weeks (for all three substrates).

Microscopy

Gram staining of smears obtained from roll tubes, and of suspensions obtained from basic flasks and serum bottles, revealed Gram negative rods ranging from 1.4 to 5.8 um in length and 0.5 to 0.7 um in width. A few of the shorter rods contained bipolar granules. A number of Gram negative cocci (<0.6 um in diameter) and Gram positive cocci (0.6 um in diameter) were also observed. No Gram positive rods were present.
Phase-contrast microscopy of agar drop preparations revealed rods ranging from 1.3 to 6.5 um in length and 0.6 um in width. Some rods contained numerous granules ranging from 3 to 6 per cell. A few rods with terminal spores were slightly curved and arranged in pairs. In preparations obtained from the Toronto Harbour site rods predominated over cocci, whereas in preparations from the Humber Bay site the organisms appeared to be more evenly distributed.

DISCUSSION AND CONCLUSIONS

Earlier research regarding biodegradation of xenobiotics involved mostly aerobic systems since it was assumed that aerobic organisms have a much more versatile metabolism than anaerobes. Recent improvements in anaerobic methodology have made it possible to more easily examine these systems in environmental studies. Microorganisms in lake sediment, where pollutants accumulate, can exist in an anoxic state, especially in the lower layers. Numerous studies presenting valuable data have now been published. These studies have focussed attention on novel metabolic pathways of anaerobic organisms. There are other, more practical reasons for the heightened interest in anaerobic degradation: it is cost-effective and methane can be recovered as a useful product.

Testing of gas production at different substrate concentrations showed that the ideal concentrations 25, 50, 100 and 200 ug C/ml. The optimum concentration was considered to be 100 ug C/ml; both 25 and 200 ug C/ml retarded gas production in some cases, whereas 50 ug C/ml in most cases gave lower gas volumes than 100 ug C/ml. Thus, the concentration of 100 ug C/ml was used for all enrichment cultures and for samples used in HPLC and gas chromatography.

All monohalogenated compounds tested were degraded to some extent by basic cultures, but the polyhalogenated compounds tested were not, as determined by gas production (Table 2). This could be due to the fact that polyhalogenated compounds require a long lag period before they are degraded, or simply because the microorganisms in the sediment were not initially acclimated. Suflita et al (1982) had found that 3,5-dichlorobenzoate and 4-NH_2 -3,5-dichlorobenzoate were less susceptible to dehalogenation than monohalogenated derivatives. Gas production was also observed in unamended test bottles (without test compound), thus pointing out that sediment organisms were able to utilize compounds indigenous to the sediment. Thus, it is possible that the halogenated compound could be degraded by one or more species present in the sediment, while being aided in its metabolism by one or more other species simultaneously growing on compounds in the sediment. This is in agreement with a recent finding by Quenson (Quenson, J., personal communication), who noted higher gas production and a shorter lag period in cultures supplemented with an abiotic extract from the original sediment. Variability in gas production, gas production in unamended cultures and net negative gas production with some substrates, conveys the idea that biodegradation may depend on a number of species, interdependent in their metabolism. The relatively high values of methane expressed as % of theoretical production, obtained from the three basic cultures, as opposed to the relatively low values obtained from enriched cultures (Table 3), suggest that the sediment microorganisms not only use test compounds but also compounds in the sediment as a source of carbon.

Depletion of substrates was shown by HPLC but a pattern was revealed with regard to the use of the substrates by sediment organisms. These organisms seemed to prefer 3-iodobenzoic acid and 3-bromobenzoic acid to 3-chlorobenzoic acid (Figures 7 to 10). The same specificity was found by Suflita et al (1982), who stated that the Br and I species are more readily dehalogenated. HPLC also showed that benzoic acid was produced as a biodegradation intermediate (Figures 7 to 10), in agreement with other studies (Suflita et al, 1982, 1983; Horowitz et al, 1983) which have shown that benzoic acid is the intermediate in reductive dehalogenation. These authors further suggested that the removal of ring-substituted halogens is the initial step in the degradation process and must occur prior to the opening of the aromatic ring. A complete dehalogenation is required before a substrate can be mineralized to CH_4 and CO_2.

The ability of sediment microorganisms to acclimate to halogenated compounds would naturally be of great interest. The cross-acclimation experiment provided some insight in this direction. There was a long lag period required before substrate depletion occurred for the monohalogenated benzoates. However, once the sediment organisms were acclimated to a monohalogenated compound, there appeared to be a very short lag before dehalogenation of the polyhalogenated substrate occurred. Perhaps further studies will reveal the presence of inducible enzymes. The degradative process is a probable result of cometabolism of different species existing in a mutualistic relationship in the sediment. This is often the case with bacterial populations involved in methane production (Atlas and Bartha, 1981). The presence of various microbial forms in the sediment, as revealed by Gram staining and by phase - contrast microscopy also points to a cometabolizing community, or a consortium, not a single species.

Shelton and Tiedje (1984b) characterized the bacteria in an anaerobic consortium that mineralizes 3-chlorobenzoate. They described short Gram negative rods (*Syntropus buswellii*), a benzoate oxidizing bacterium, slightly curved, long, Gram negative rods (*Methanogen hungatei*), irregular rods with various inclusions (butyrate oxidizers), and long, thin rods (other methanogens) (Tiedje et al, 1986). A consortium may contain other major groups of obligate anaerobes, such as Clostridia (fermenters), Desulfovibrio or Desulphotomaculum species (sulphate reducers), proton reducers (oxidize fatty acids and alcohols to acetate and CO_2), and CO_2 reducers (use CO_2 as a terminal electron acceptor and create CH_4 or acetate) (Kaspar and Tiedje, 1982).

The Toronto Harbour sediment contained a large proportion of Gram negative rods. The Humber Bay sediment seemed to have a more even distribution between cocci and Gram negative rods. The Toronto Harbour sediment was clearly more metabolically active than Humber Bay sediment. The inference here is that the Gram negative rods may be able to make better use of the greater amount of organic material in the Toronto Harbour sediment, in contrast to the sandy, less organic constitution of the Humber Bay sediment. Future studies should include quantitative analyses.

In summary, our results imply that (i)in order of preference, 3-bromobenzoic acid, 3-iodobenzoic acid and 3-chlorobenzoic acid can be degraded to CH_4 and CO_2 by Lake Ontario sediment organisms with a lag period ranging from 6 to 10 weeks; (ii)the biodegradation is carried out by an anaerobic consortium of microorganisms characterized by a high proportion of Gram negative rods; (iii)the biodegradation probably proceeds via a reductive dehalogenation pathway with benzoic acid as a main intermediate; (iv)Toronto Harbour sediment microorganisms have greater biodegradative potential than those present in Humber Bay sediment; and, finally (v)cross-acclimation can lead to the degradation of more complex substrates.

The next step will be to isolate and cultivate the consortium in order to allow for possible use of such a cometabolizing community in waste water facilities. This approach would provide an almost natural mode for the biodegradation of industrial wastes prior to their release into our lake ecosystems. Later, it may be possible to isolate and purify the enzyme system(s) involved in the dehalogenation process for subsequent industrial applications. These approaches would especially be important for the degradation of more complex compounds, such as polyhalogenated benzoates, or PCB's. A long-range objective would be to fit the accumulated data to a kinetic model in order to predict the ultimate fate of persistent contaminants in Lake Ontario sediments.

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Table 1: Station locations for the 1986 and 1987 sediment collection along Toronto Waterfront

Site Location	MOE No.	Date of Sediment Collection
Humber Bay (STP*outfall)	332	July 1987
Humber Bay	335	October 1986 July 1987
Toronto Harbour	1355	October 1986 July 1987
Toronto Harbour (near Keating Channel)	1375	July 1987
Ashbridges Bay (Main STP*outfall)	A	July 1987
Eastern Beaches (R.C. Harris Filtration Plant intake)	2216	July 1987

* STP: Sewage Treatment Plant

Table 2: Cumulative total gas production as measured by pressure transducer (1986 sampling)

Site:	Humber Bay				Toronto Harbour			
Substrate	vol (ml)	time (d)	conc[1] (ug C/ml)	conc[2]	vol (ml)	time (d)	conc[1] (ug C/ml)	conc[2]
4-NH_2-3,5-diClBZ	negative				negative			
3,5-diClBZ	negative				negative			
3-ClBZ	negative				8	70	50	
3-BrBZ	negative				26	85	200	25,50
3-IBZ	negative				30	70	200	25,50
BZA	negative				30	72	200	50
Ethanol	35	80	200	25	33	60	200	25
Phenol	50	80	200	25	not tested			
Cresol	20	50	200		not tested			

vol: maximum net gas volume produced (net gas volume was obtained by subtracting volume produced in unautoclaved control bottles from that produced in test bottles)

d: the number of days of incubation needed for maximum net gas volume to occur

ug C/ml: micrograms of carbon (substrate) per milliter of slurry + RAMM

conc[1]: concentration of substrate at which maximum net gas production occurred

conc[2]: concentration of substrate at which gas production was not detectable

Table 3: Production of methane as measured by gas chromatography and its relation to theoretical methane production (obtained by the Buswell equation)

Test Chemical	Site	Type of Culture	Methane Volume (ml)	Methane as % of Theoretical Methane Production
3-IBZ	Toronto Harbour	Enriched	46.0	49.7
3-IBZ	Toronto Harbour	Enriched	42.3	45.7
3-BrBZ	Toronto Harbour	Enriched	34.1	36.8
3-BrBZ	Toronto Harbour	Enriched	40.6	43.9
3-ClBZ	Toronto Harbour	Enriched	6.3	6.8
3-ClBZ	Toronto Harbour	Enriched	5.2	5.7
3-IBZ	Humber Bay	Basic	106.4	115.0
3-BrBZ	Humber Bay	Basic	136.5	147.6
3-ClBZ	Humber Bay	Basic	108.9	117.7

Table 4: Degradation of substrates in terms of preference (most completely degraded substrate first) as monitored by high pressure liquid chromatography

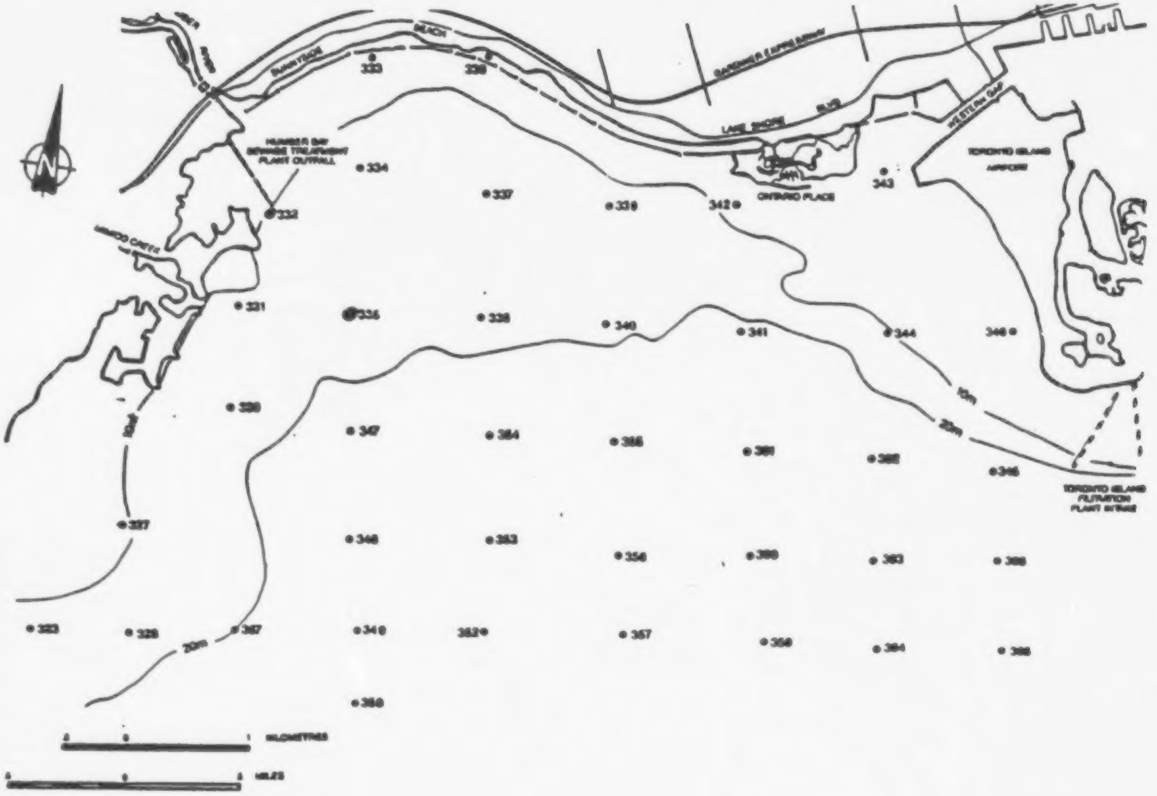
Site	Type of Culture	Substrates
Toronto Harbour	Enriched	3-BrBZ, 3-IBZ, 3-ClBZ
Toronto Harbour	Basic	3-BrBZ, 3-IBZ, 3-ClBZ
Humber Bay	Enriched	3-IBZ, 3-ClBZ, 3-BrBZ
Humber Bay	Basic	3-IBZ, 3-BrBZ, 3-ClBZ

LEGEND FOR FIGURES

Fig. 1	Humber Bay sediment collection sites along Toronto Waterfront. Site 332 (1986 sampling) and site 335 (1986 and 1987 samplings).
Fig. 2	Toronto Harbour sediment collection sites along Toronto Waterfront. Site 1355, near marina entrance (1986 and 1987 samplings) and site 1375, near Keating Channel (1987) sampling.
Fig. 3	Ashbridges Bay sediment collection site along Toronto Waterfront. Site "A" (1987 sampling), near Main Sewage Treatment Plant outfall.
Fig. 4	Eastern Beaches sediment collection site along Toronto Waterfront. Site 2216 (1987 sampling), near R.C. Harris Filtration Plant intake.
Fig. 5	Net gas production measured by pressure transducer. 1986 samling, site 335(Humber Bay). All values showed negative gas production. Cultures were incubated in the presence of (A) 4-NH_2-3,5-diClBZ, (B) 3-ClBZ, (C) 3-BrBZ, (D) 3-IBZ.
Fig. 6	Net gas production measured by pressure transducer. 1986 sampling, site 1355(Toronto Harbour). Some substrate concentrations resulted in positive gas production. Cultures were incubated in the presence of (A) 3-ClBZ, (B) 3-BrBZ, (C) 3-IBZ.
Fig. 7	Pattern of substrate disappearance as revealed by HPLC. Analysis of 1986 sampling (site 1355, Toronto Harbour) cultivated in enriched culture. A. Comparison of the three substrates, 3-ClBZ, 3-IBZ, 3-BrBZ. B., C., D. Comparison of each substrate with level of benzoic acid (BZA), dehalogenation intermediate.
Fig. 8	Pattern of substrate disappearane as revealed by HPLC. Analysis of 1986 sampling (site 335, Humber Bay) cultivated in enriched culture. A. Comparison of the three substrates, 3-ClBZ, 3-BrBZ, 3-IBZ. B., C., D. Comparison of each substrate with level of benzoic acid (BZA), dehalogenation intermediate.
Fig. 9	Pattern of substrate disappearance as revealed by HPLC. Analysis of 1986 sampling (site 1355, Toronto Harbour) cultivated in basic culture. A. Comparison of the three substrates, 3-ClBZ, 3-BrBZ, 3-IBZ. B., C., D. Comparison of each substrate with level of benzoic acid (BZA), dehalogenation intermediate.

LEGEND FOR FIGURES

Fig. 10 Pattern of substrate disappearance as revealed by HPLC. Analysis of 1986 sampling (site 335, Humber Bay) cultivated in basic culture. A. Comparison of the three substrates, 3-ClBZ, 3-BrBZ, 3-IBZ. B., C., D. Comparison of each substrate with level of benzoic acid (BZA), dehalogenation intermediate.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LAKE SHORE BLVD
WESTERN GAP
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TORONTO ISLAND AIRPORT
HUMBER BAY SEWAGE TREATMENT PLANT OUTFALL
MIMICO CREEK
TORONTO ISLAND FILTRATION PLANT INTAKE
10m
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333
334
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fig.1

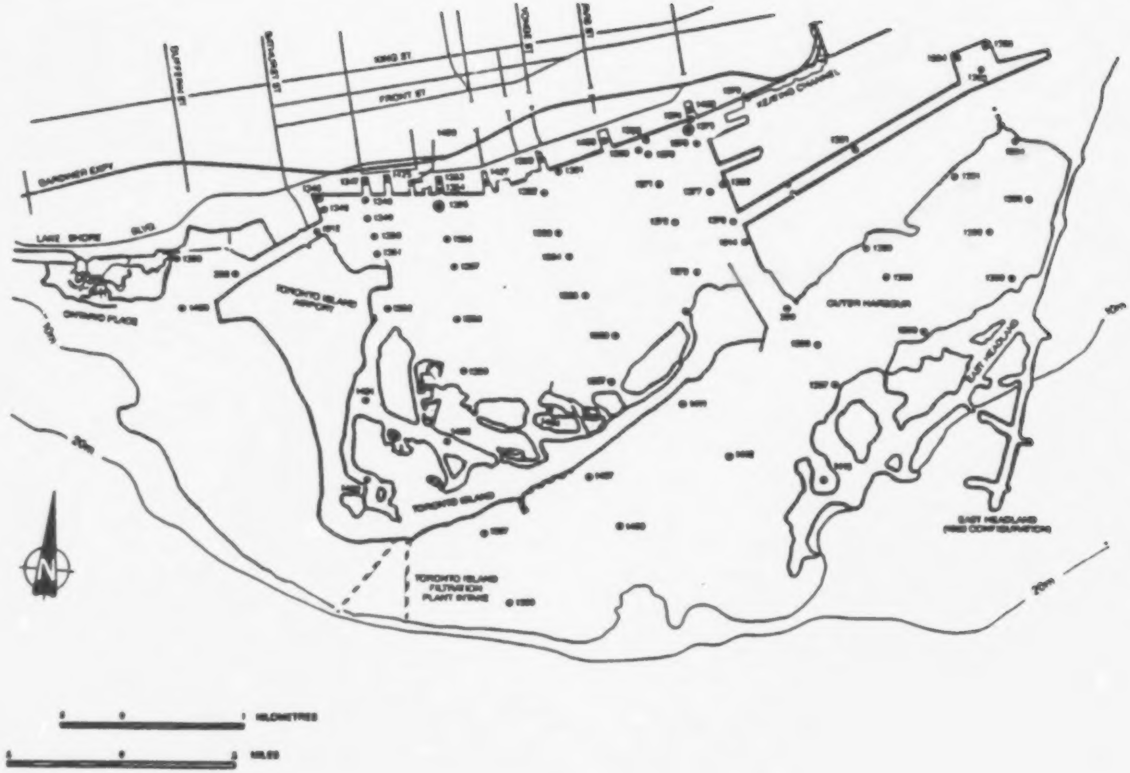
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fig. 2

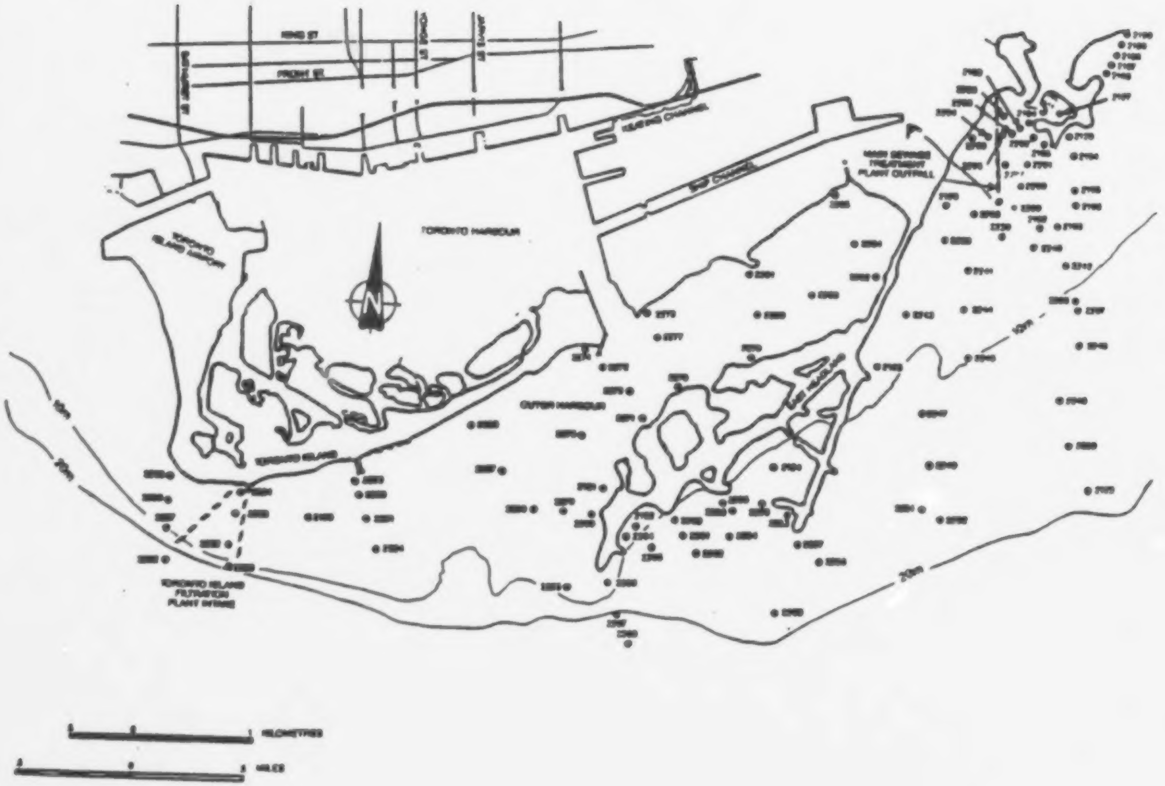
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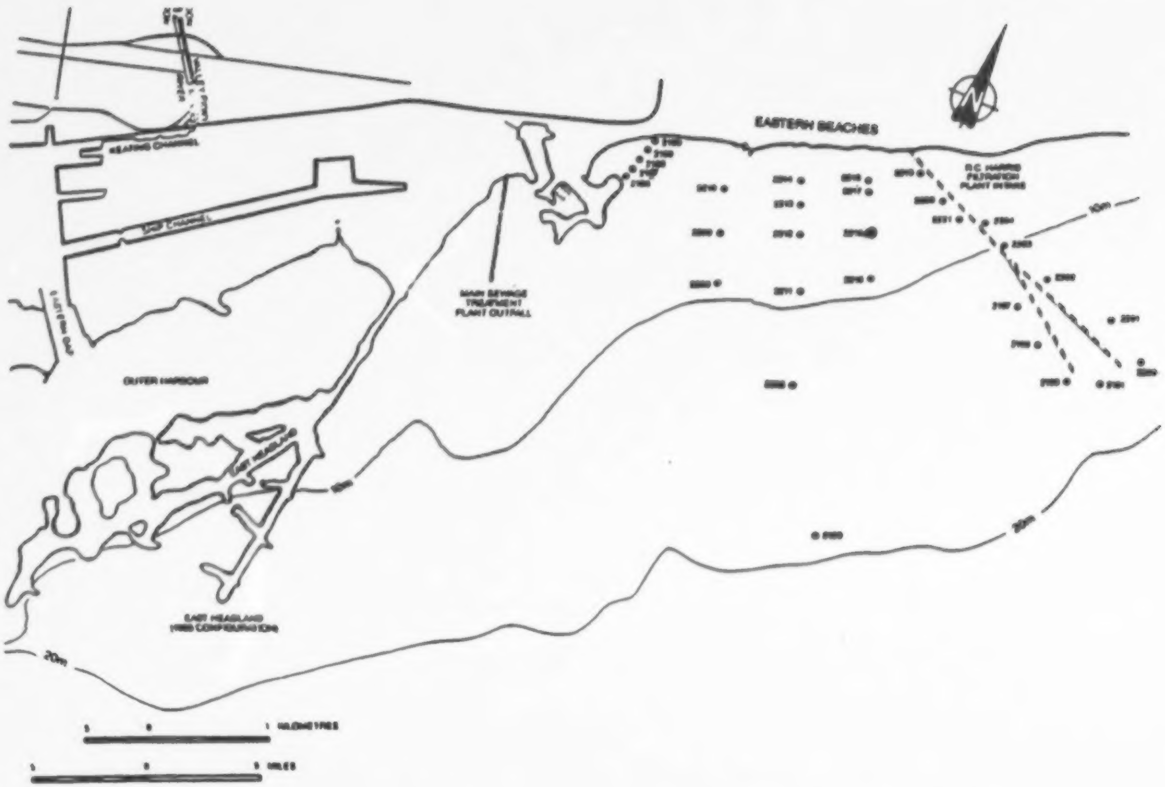
fig. 3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R.C. HARRIS
FILTRATION
PLANT INTAKE
MAIN SEWAGE
TREATMENT
PLANT OUTFALL
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fig. 4

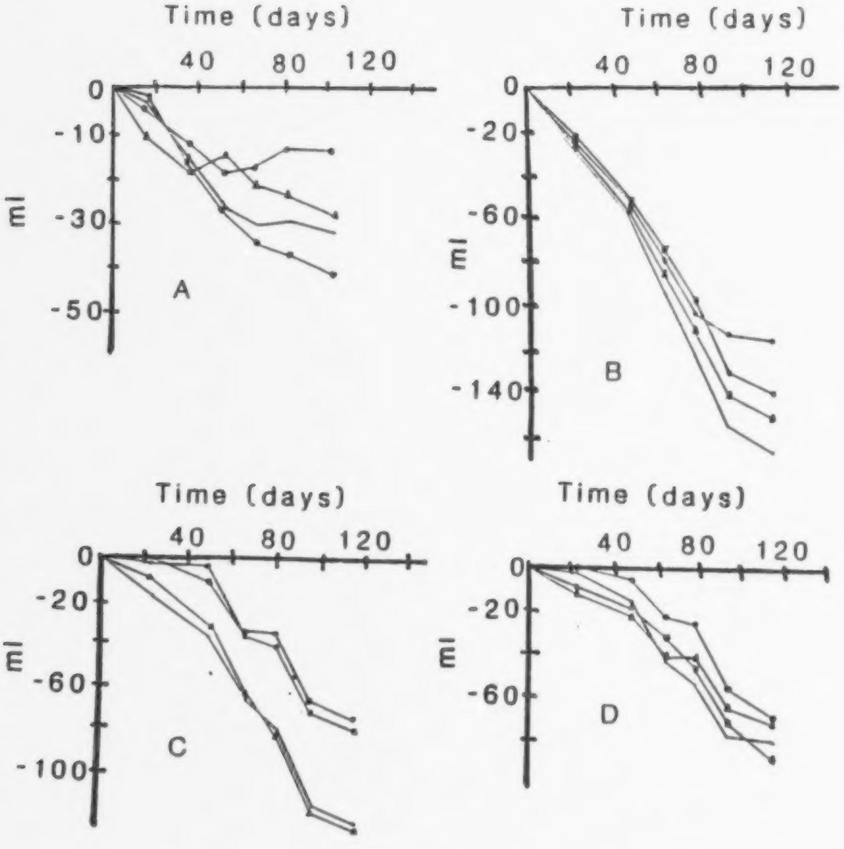
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fig. 5

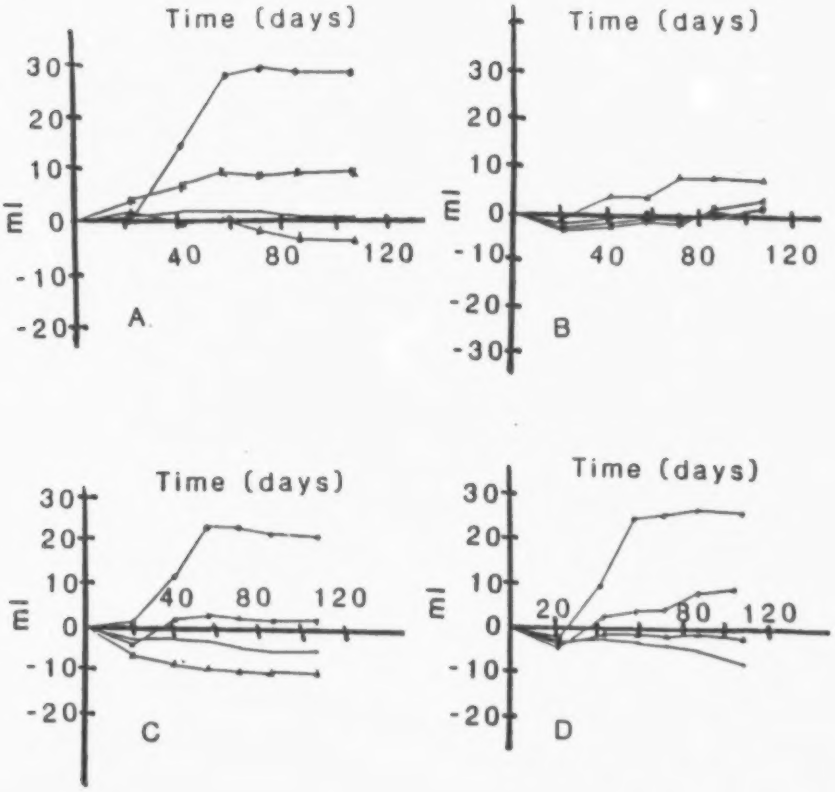
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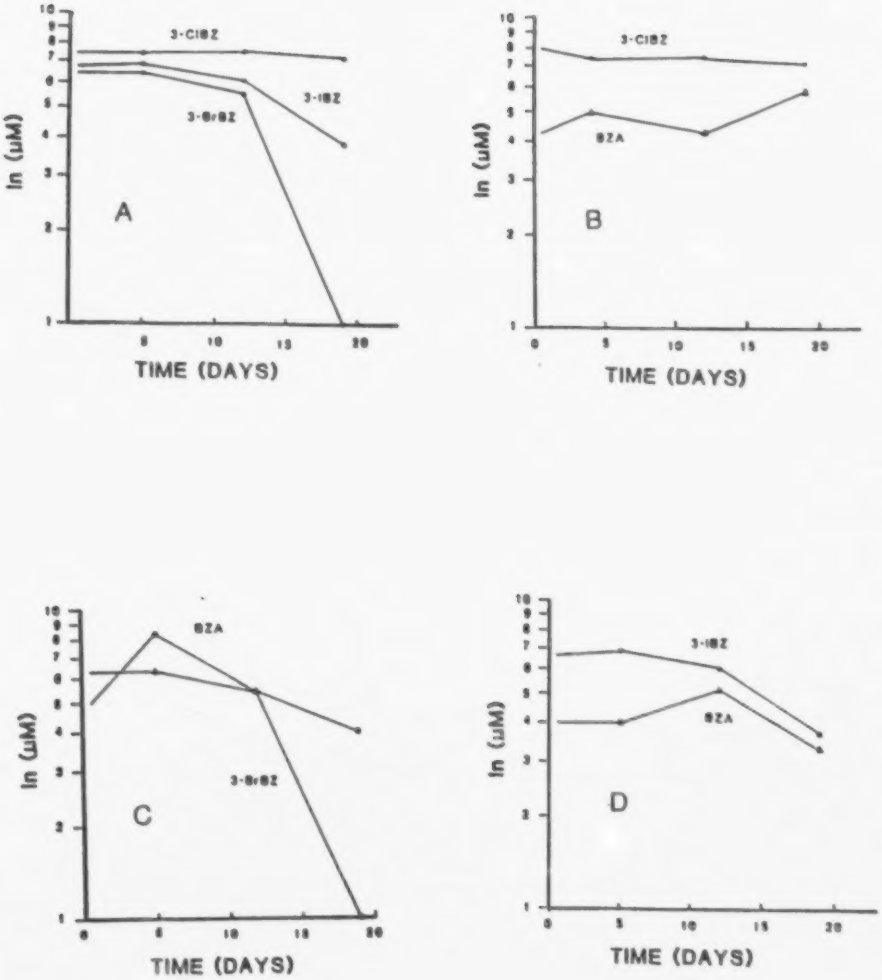
fig. 6


3-ClBZ
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3-BrBZ
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ln (μM)
TIME (DAYS)
3-ClBZ
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3-BrBZ
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D
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fig. 7

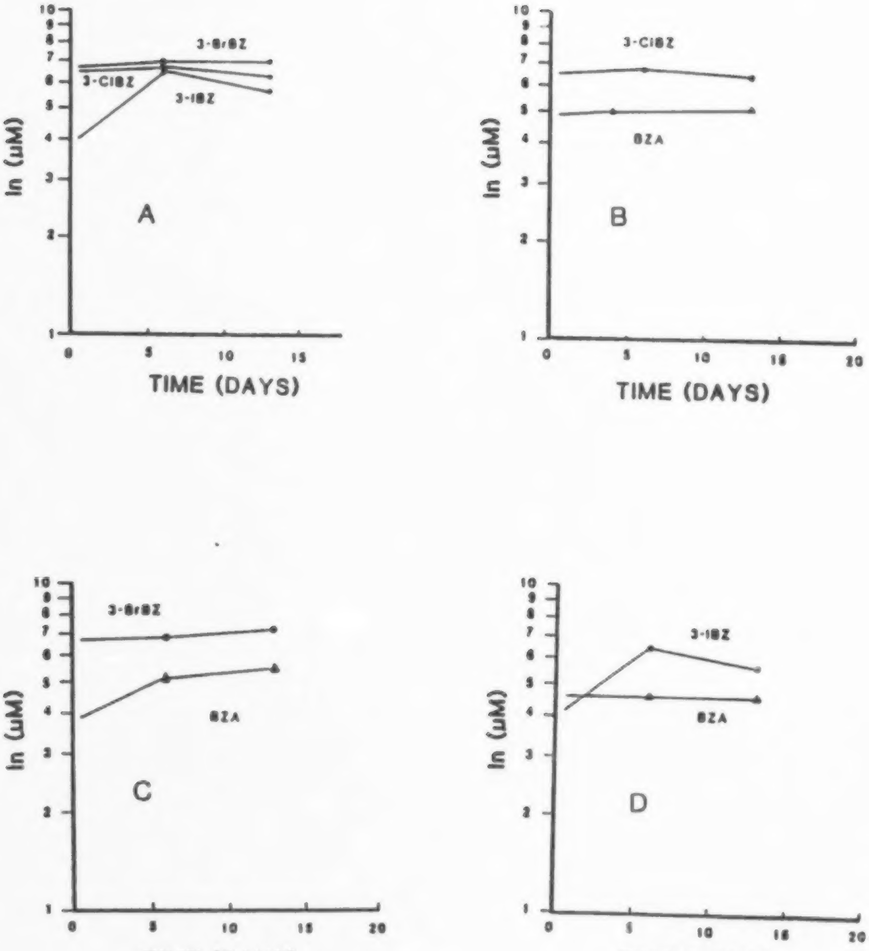A
B
C
D
3-BrBZ
3-ClBZ
3-IBZ
BZA
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fig. 8

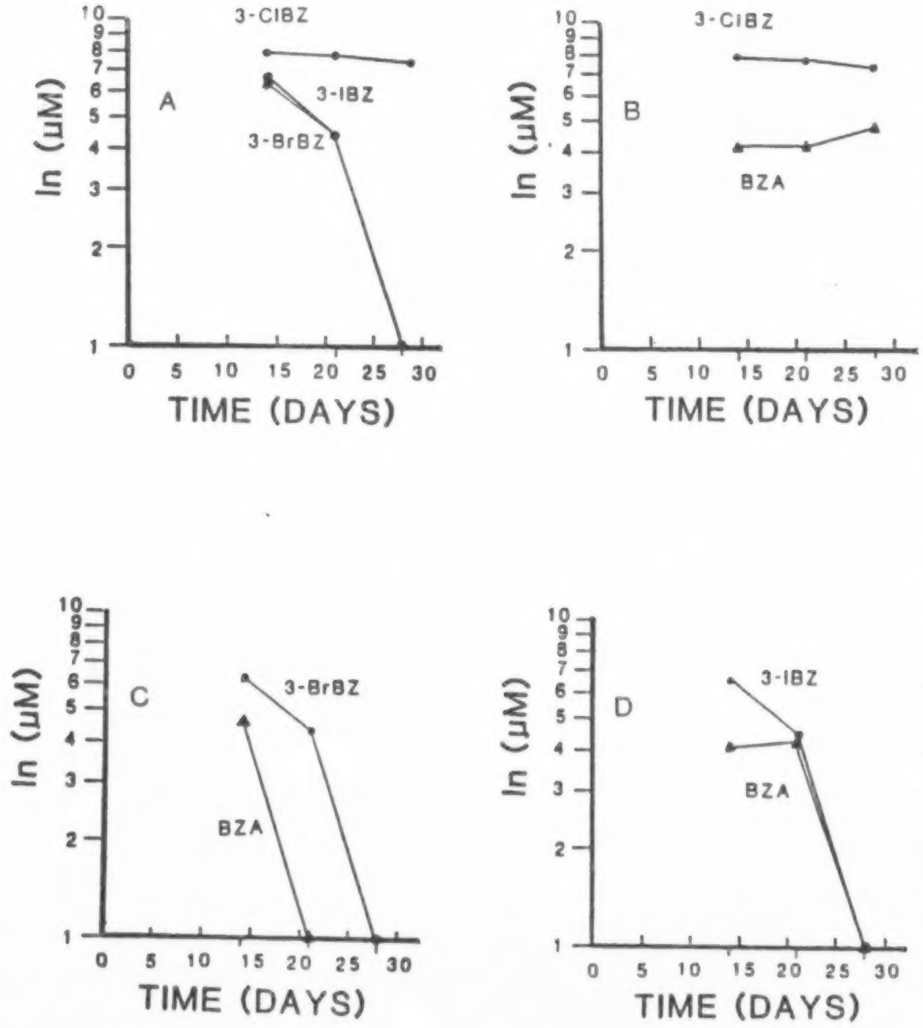
A
3-ClBZ
3-IBZ
3-BrBZ
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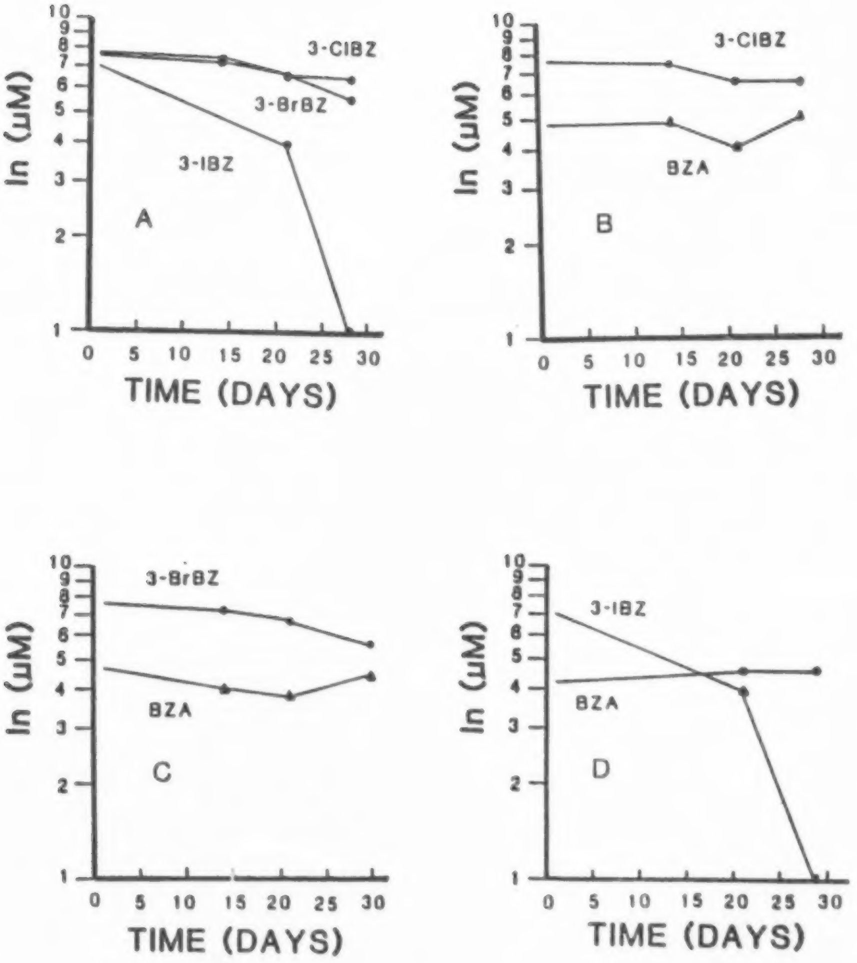
fig. 9



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TIME (DAYS)
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25
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fig. 10

The Effect of Tile Drainage and Ditches
on Peak Flows and Dry Weather Flows

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Department of Civil Engineering

Queen's University at Kingston

Ministry of the Environment Research Project #152 PL

ABSTRACT

The objective of the research described in this summary paper was to investigate the hydrology of the agricultural drainage process and its impacts on the land phase of the hydrologic cycle. Statistical tests were performed on flow data in an attempt to identify trends in the data which could be attributed to the drainage process. Additionally, the impacts of both tile drainage at the field level and ditch drainage at the small basin level were considered and analyzed through the use of a physically-based hydrologic model capable of simulating the drainage process continuously through the frost-free period. Required input included field and tile geometry (field length and slope, number and spacing of drain tiles, depth of tile), soil characteristics (depression storage capacity, depth of ploughed layer and depth to impervious layer), groundwater parameters (saturated hydrologic conductivity and drainable porosity), and meteorological data (hourly rainfall and mean daily temperature). Output included soil moisture storage, groundwater table height, subsurface hydrograph and contribution to surface runoff. The model was tested and calibrated on two fields in southeastern Ontario.

INTRODUCTION

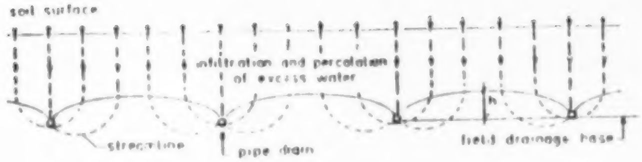
Overview of Agricultural Drainage

Agricultural land drainage enhances the natural drainage process to remove excess water from farmland, thus increasing its productivity. In Ontario, two levels of agricultural drainage works can be identified: tile or ditch drains at the field level, and municipal drains.

Tile drainage consists of a network (usually systematically controlled) of clay tiles or, more commonly, perforated plastic pipe, installed at a uniform depth below the crop root zone. Excess water percolates downwards and moves under the influence of gravity to the drain, where it is removed from the field (Figure 1). The drains effectively keep the ground water table below the root zone, allowing aeration of the root zone, and preventing stress to the crop. In addition, the tile drains lower the spring water table more rapidly than would natural interflow or evaporation - thus allowing the farmer access to his field for earlier harrowing and seeding.

Municipal drains are either new or improved existing channels which convey the excess water from the fields to receiving creeks or rivers.

Because less than five percent of the total land in Canada is suitable for cultivation, the reclamation of cultivable land by drainage improvement will continue to accelerate. The effects of this drainage on those rivers and streams that receive waters from drained areas are not clearly understood, but they can be adverse. In particular, they may include increased peak flows and reduced low flows. Increased peak flows cause erosion and flooding, and downstream landowners often demand expensive flood control structures to restore pre-drainage flood levels. Reduced low flows result in impaired water quality conditions and downstream users may


soil surface
infiltration and percolation of excess water
h
streamline
pipe drain
field drainage base

Typical flow pattern to parallel pipe drains

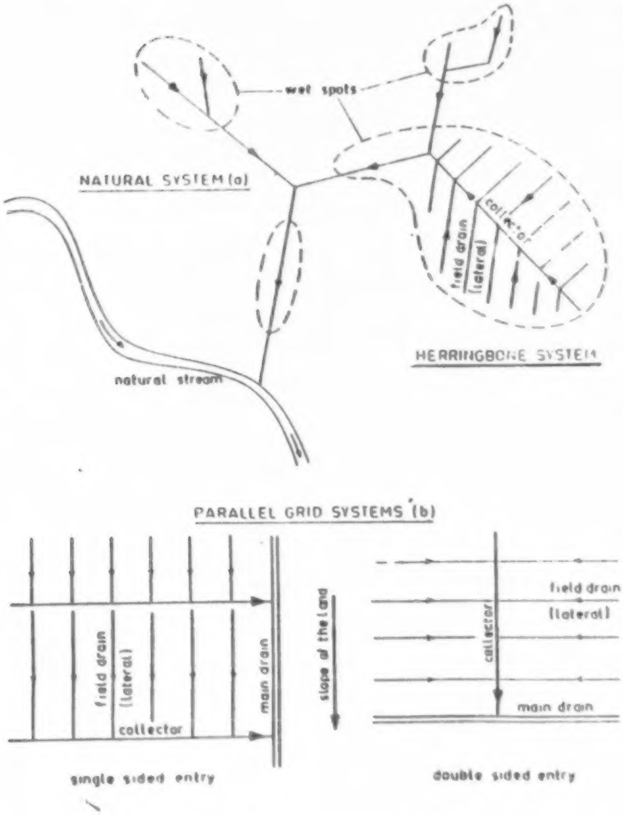

wet spots
NATURAL SYSTEM (a)
collector
field drain (lateral)
HERRINGBONE SYSTEM
natural stream
PARALLEL GRID SYSTEMS (b)
field drain (lateral)
collector
main drain
slope of the land
single sided entry
field drain (lateral)
collector
main drain
double sided entry

Figure 1 Illustration of tile drainage (Smedema et al. 1983)

demand expensive water storage structures to increase low flows to pre-drainage conditions. Concerns over both these effects has resulted in pressure to delay, defer and cancel drainage projects. However, there is no general agreement on the hydrologic impacts of tile drainage, and often claims by both proponents of, and objectors to, drainage projects are speculative.

Because of the lack of understanding of the overall hydrologic response to agricultural drainage, there is an urgent need for research to evaluate the impacts of drainage and for the dissemination of knowledge as it becomes available to assist in the planning of drainage projects which are technically, environmentally, and economically sound.

Objectives of the Study

In order to increase the understanding of the hydrologic behaviour of tile drainage the following objectives were defined:

- perform statistical analyses to detect the effects of agricultural drainage on peak flow and dry weather flow;

- develop, test and calibrate a physically-based model which is capable of simulating the hydrologic response of agricultural drainage on a basin scale;

- undertake field studies to calibrate and test the model; and

- use the model to evaluate the effects of tile drainage and open ditches on peak flows and dry weather flows.

STATISTICAL ANALYSIS OF FLOW TRENDS IN DRAINED AREAS

General Approach

The use of trend analysis to detect changes in the hydrological cycle as a result of drainage activity requires the examination and comparison of two data sets. First, streamflow records with a sufficiently long period of record during the drainage activities must be located and then analyzed for trends in flow peaks, low flow levels and durations, and other hydrological anomalies which might be attributable to drainage activity. Secondly, if trends are found (or even if they are not), a comparison of the flow series should be made to some index of drainage activity with time. Unfortunately, this latter time series is somewhat difficult to derive. Although the Ontario Ministry of Agriculture and Food maintains an agricultural resource inventory which includes township maps detailing artificial drainage systems (both municipal drains and tiled fields are identified), these maps provide only one point on the required drainage intensity index time series.

To minimize the unnecessary expenditure of time and to avoid the development of several drainage intensity indices which may not be required, the researchers adopted the following approach.

1. Uncontrolled streams and rivers in agricultural areas having a sufficient period of flow records to permit a trend analysis were identified.

2. If a trend was identified, climatic records were examined to identify a climatological trend which could account for the trends in flow records.

3. Drainage intensity time series would be developed only if flow trends could not be accounted for by climatalogical trends.

4. The drainage intensity time series would be examined to determine a causal relationship with the flow records over the same time period.

Following an examination of the Historical Summary of Streamflow Records (Environment Canada 1983) the gauging stations listed in Table 1 were identified as potential candidates for trend analysis. The statistical analyses concentrated on an examination of two time series: summer mean daily flows and hydrograph recessions.

Table 1 Candidate stations for trend analysis

WSC No.	Station Name
02FF002	Ausable River near Springbank
02FC001	Carrick Creek near Carlsruhe
02HC009	East Humber River near Pinegrove
02GD010	Fish Creek near Prospect Hill
02GC002	Kettle Creek at St. Thomas
02GD008	Medway River at London
02GD004	Middle Thames River at Thamesford
02FE004	Maitland River near Donnybrook
02GA018	Nith River at New Hamburg
02GA010	Nith River near Canning
02LB007	South Nation River at Spencerville
02FB007	Sydenham River near Owen Sound
02GG002	Sydenham River near Alvinston
02HA006	Twenty Mile Creek at Balls Falls

Summer Flow Analysis

The examination of summer flows involved the periods from June to November inclusive.

Because it was the higher flows and lower flows in the summer period that were of primary interest, the flow data were analyzed first to define the mean flow and the upper and lower quantiles of mean daily flow. The number of days in each year with flows above the upper quantile and below the lower quantile flow value were identified and summed. The number of days of high flow and low flow were ranked and a Spearman rank order correlation coefficient test for trend was performed. The intent of the test was to ascertain whether the number of low or high flow days was increasing or decreasing significantly over the period of record.

For virtually all the rivers tested, a significant trend was identified. This trend showed a reduction with time in the number of days in each year with flows below the lower quantile value. Similarly, although less significant, an increase in the number of higher flow days (flow values above the upper quantile value) was noted.

Trends with Precipitation

Short term climatological changes over the period of record may have induced trends in the precipitation volumes which would affect runoff volumes. For example, a positive trend in precipitation volumes could have led to the observed decrease in the number of low flow days with time. The Woodstock climatological station was selected as a representative station in southwestern Ontario, and a trend analysis was performed on summer precipitation volumes from 1946 to 1982. A Spearman test for trend with a rank order correlation coefficient indicated a significant positive trend over the period of record.

This brief analysis indicates that the influence of precipitation trends on streamflow cannot be ignored, and in fact the precipitation variability likely masks any other more subtle influences on streamflow, such as tile drainage. A more detailed analysis of precipitation trends in the London area was performed by Serrano et al. (1985). Through analysis of 5-year moving averages of precipitation amounts and streamflow on the Middle Thames watershed, these investigators demonstrated "the lack of trend of streamflow with time due to any cause other than variation in mean precipitation".

Hydrograph Recession Analysis

If the drainage process significantly alters the watershed storage and transmission elements so as to remove water more rapidly from the land, this impact should be evident in the recession limbs of hydrographs following rainfall events (Figure 2).

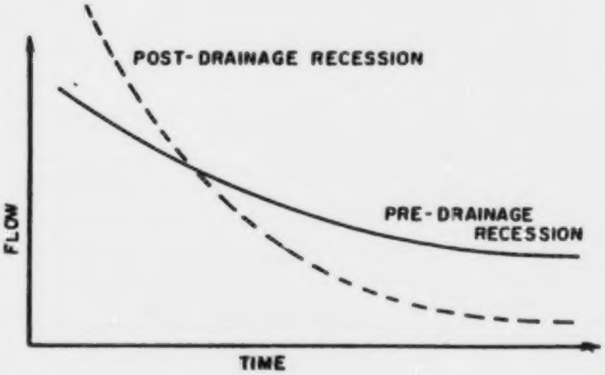


Figure 2 Hydrograph Recessions - drained versus undrained

To analyze this effect, the split records of daily flows (first half and latter half of the period of record) were subjected to an autocorrelation analysis at lags of one to twenty-five days. If drainage effects were significant, flows from the first half (less drainage) should exhibit more persistence (i.e. higher autocorrelation) than records from the second half, because of shorter travel times and limited system memory in the drained case.

Following this analysis for the rivers in Table 1, no consistent significant trend for the rivers under study, was identified. Autocorrelation functions for the Middle Thames River at Thamesford are illustrated in Figure 3.

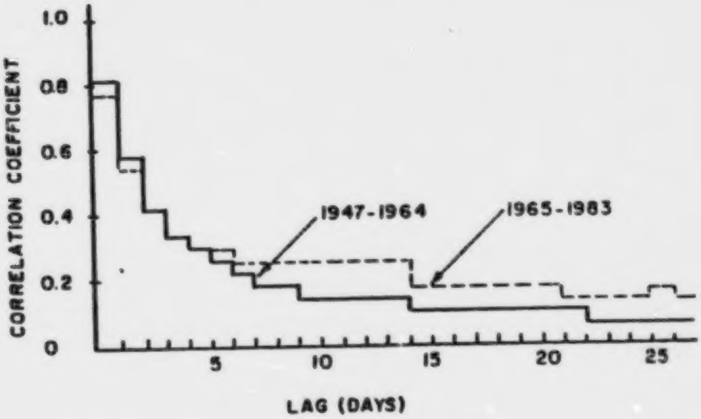


Figure 3 Autocorrelation function - Middle Thames River annual flow series

Trend Analysis Summary

Brief comments regarding the preliminary work performed for the examination of trend in the flow records are noted as follows.

1. The findings are inconclusive; either the effects of drainage are secondary or they are compensating. Effects of tile versus surface drainage may counteract each other once flows enter the receiving stream, and changes in the synchronization of various runoff peaks within a watershed may obscure individual field level or subbasin effects. Finally, individual runoff events may behave differently under drainage but the net runoff frequencies and volumes may be relatively unchanged.

2. Any trends or differences are easily masked by larger scale physical or climatological changes, such as short term trends in precipitation volumes or low flow releases from river regulation.

3. Any examination of flow records for trend is time consuming and expensive in man hours and computer time. In addition, selection of the model for testing is difficult because the actual processes and their possible effects are unknown. Without understanding the processes, except for general conceptualizations, it is difficult to be objective and to establish a definitive test identifying trend and its causative factors.

4. The above noted item can be extended to cover any trends that may be identified. Uncertainty will exist in defining the causative factors of the trend and ascertaining whether it is due to drainage or other physical factors, or is an artifact of the data manipulation process.

As a result of the preliminary analysis for trend, the need to understand the drainage process at the field level on an event by event basis was reinforced. Further efforts on the project were directed to the simulation of drainage through the development and application of a physically-based tile drainage model.

FIELD STUDIES

The Test Fields

Tile runoff data was collected from two test fields to assist in the development of the model and to provide data for calibration and verification. During 1985 and 1986, the two tiled fields were instrumented for rainfall and tile discharge (Figure 4): the 14 ha Leclerc Field near Ottawa which has sandy loam soil, and the 15 ha Napanee Field near Kingston, which has a clay soil overlying limestone bedrock.

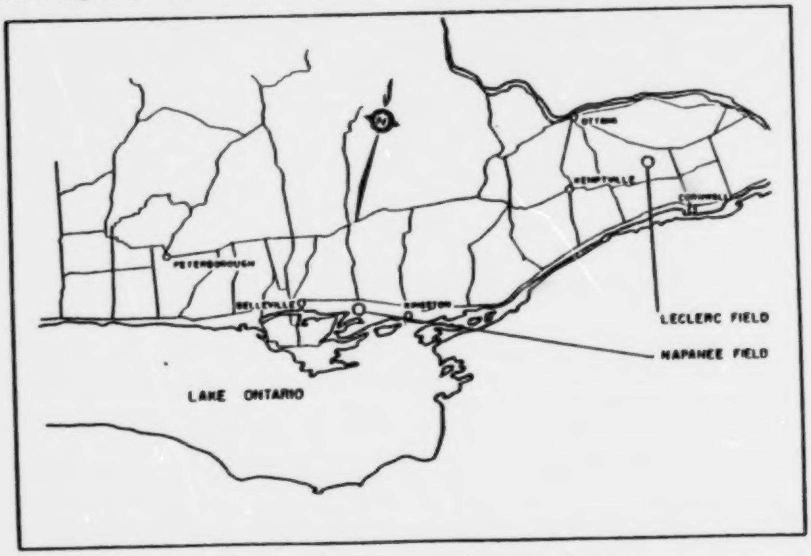

N
OTTAWA
KEMPTVILLE
CORNWALL
PETERBOROUGH
BELLEVILLE
KINGSTON
LECLERC FIELD
NAPANEE FIELD
LAKE ONTARIO

Figure 4 Locations of instrumented fields

The Leclerc field has tiles spaced at intervals of 16.8 metres. A Stevens type F recorder was used to monitor the water level in a collection tank with a compound V-notch weir. A chart recording, tipping bucket rain gauge was located within 500 m of the field. Water levels over the weir and rainfall rates were recorded continuously from May 1985 to November 1985 and again from May to December 1986.

Instrumentation on the Napanee field (Figure 5) included a collection tank with a compound V-notch weir at the tile outlet. Water levels over the weir were recorded continuously from April to December 1986 with the use of a Stevens A-71 chart recorder at a 1:1 recording ratio and a speed of 6.0 cm/day. Rainfall volumes and rates were also recorded with a tipping bucket rain gauge and a continuous strip chart recorder (Weather

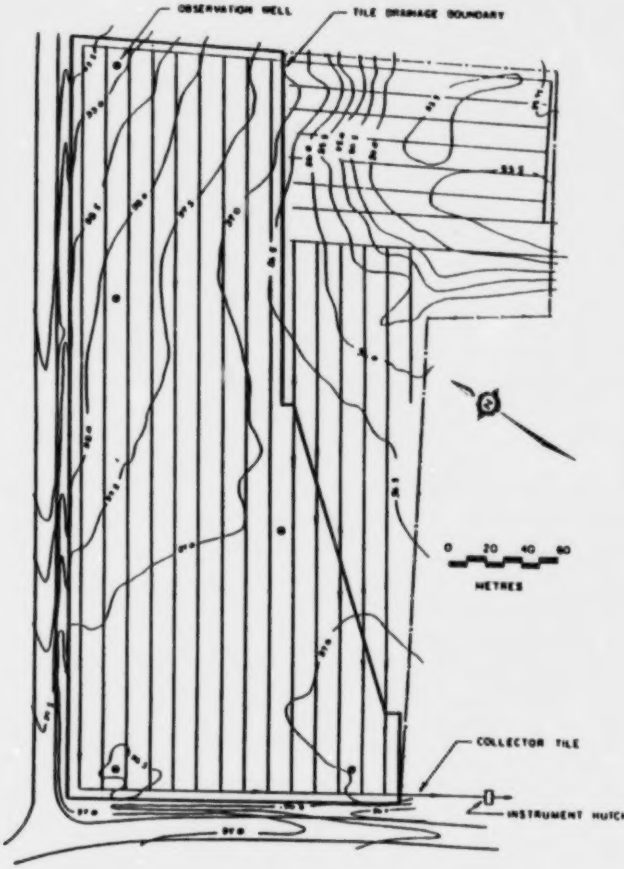

OBSERVATION WELL
TILE DRAINAGE BOUNDARY
0 20 40 60
METRES
COLLECTOR TILE
INSTRUMENT HUTCH

Figure 5 The Napanee field

Measure Corporation Model P522). Five observation wells consisting of 100 mm ABS pipe, sleeved in filter fabric were installed to allow periodic measurements of watertable elevation. A summary of the larger rainfall events recorded on the two test fields is presented in Tables 2 and 3.

Table 2 Summary of storm events - Napanee Field

Date (1986)	Rainfall (mm)	Tile Runoff (mm)	Peak Tile Flow (m^3/s)	Surface Flow (mm)*
Apr 15-21	23.4	13.4	0.0038	0
May 19-23	89.8	31.7	0.0117	18.2
June 11-16	71.4	28.7	0.0124	3.5
Aug 15-18	19.0	0.6	0.0003	0
Sept 10-16	90.4	35.8	0.0122	13.2
Sept 22-28	36.4	22.8	0.0122	3.5
Sept 29-06	56.8	36.1	0.0118	0
Oct 12-16	22.0	11.2	0.0063	0

* simulated

Table 3 Summary of storm events - Leclerc Field

Date (1986)	Rainfall (mm)	Tile Runoff (mm)	Peak Tile Flow (m^3/s)	Surface Flow (mm)*
May 19-24	45.4	7.1	0.0056	0
July 03-08	40.9	2.5	0.0029	0
Sept 23-26	12.2	2.7	0.0044	0
Sept 29-07	50.0	22.5	0.0119	0
Oct 12-18	19.3	14.4	0.0102	0
Oct 26-30	26.3	6.4	0.0075	0

*simulated

Field Studies Program - Napanee Field

The Napanee field (Figure 5) was also the subject of a comprehensive field studies program for the determination of the field's physical properties. The topographic survey of the field shows it to be gently sloped in a north-south direction with the slopes ranging from 0.0008 to 0.001 m/m. The limestone bedrock is not at a constant elevation under the field, but varies in depth from approximately 0.6 m along the northern edge to approximately 2.0 m at the southern end. The soil is a Lansdowne clay (Gillespie et al. 1963) overlying an Ordovician limestone. The tiles are spaced at 12.2 m and define a subsurface drainage area of 5.04 ha.

Soil moisture measurements were taken throughout the summer months to ascertain the initial soil moisture content of the field prior to rainfall events. Bulk density measurements were taken and an extensive testing program was conducted to determine the hydraulic conductivity and drainable porosity at various depths and locations throughout the field. Additional detail on the field measurement techniques and analyses may be found in Whyte (1987).

Tests to determine saturated hydraulic conductivity included the auger hole method during periods when the water table was near the surface, and use of the Guelph permeameter when the water table was below the drain tiles. In addition, under saturated conditions with the water table at the surface of the field, Hooghoudt's equation for tile discharge (Hooghoudt 1940) was used to determine an integrated field effective value of saturated hydraulic conductivity from the tile drainage system performance.

Average drainable porosity represents the maximum water available through gravity drainage and is the difference between saturated moisture content and field capacity. It was determined directly from the field drainage data following a method outlined by Taylor (1960) which involves integration of the recession limb of the tile discharge hydrograph and relating this volume to the drop in the groundwater table over the same time period. This field technique tends to integrate variations in drainable porosity which could arise due to minor differences in soil type over the field.

TILED FIELD SIMULATION MODEL

Introduction

TILE is a physically-based model designed to simulate the hourly hydrologic responses of an agricultural field subjected to tile drainage. Processes modelled are infiltration, filling depression storage, percolation of infiltrated water into the root zone and the lower zone, groundwater flow and evapotranspiration from the soil surface and lower zone. Algorithms used to represent these processes are relatively simple and are compatible with the levels of accuracy possible in measuring the physical characteristics and parameters of the fields being simulated.

Figure 6 illustrates the systematically tile drained field which TILE is capable of modelling. Also illustrated is the method of defining an equivalent tile lateral length for situations where the systematic drainage has varying tile lengths. The model is not suited for accurately modelling random or dendritic type drainage schemes. A detailed discussion of the model development and its algorithms is given by Watt and Paine (1987).

Model Calibration and Verification

Using information from the field studies program and typical ranges of physical parameters from the literature, the model was calibrated on one half of the available events from each field and verified on the remaining events. Calibration concentrated on matching the observed tile runoff volume, the observed peak discharge, and the time to peak. Water table observations were not used because they were not taken on the Leclerc field and were not performed continuously for the Napanee field.

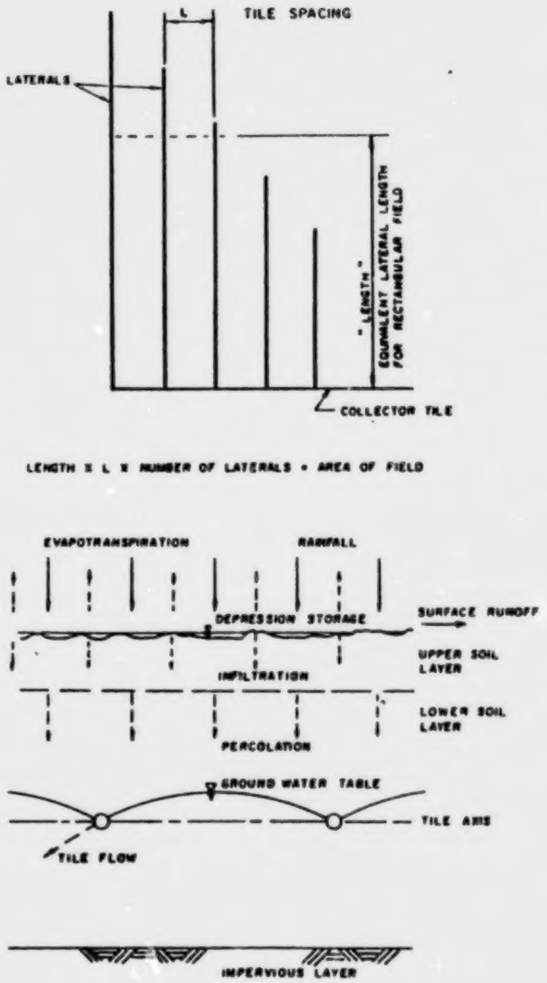

L
TILE SPACING
LATERALS
"LENGTH" EQUIVALENT LATERAL LENGTH FOR RECTANGULAR FIELD
COLLECTOR TILE
LENGTH X L X NUMBER OF LATERALS = AREA OF FIELD
EVAPOTRANSPIRATION
RAINFALL
DEPRESSION STORAGE
SURFACE RUNOFF
UPPER SOIL LAYER
INFILTRATION
LOWER SOIL LAYER
PERCOLATION
GROUND WATER TABLE
TILE AXIS
TILE FLOW
IMPERVIOUS LAYER

Figure 6 The physical system - a systematically tile drained field

Reasonably satisfactory results were obtained for the fields for both the volume of tile discharge and the peak tile flow (Figure 7). Agreement between simulated and observed tile flow for the Leclerc field, with its rapidlydraining sandy loam, was somewhat better than that for the Napanee field. The recession limb of the tile flow hydrograph for the Napanee field was difficult to fit, suggesting that the approximation of the groundwater discharge and storage relationship to a linear reservoir may

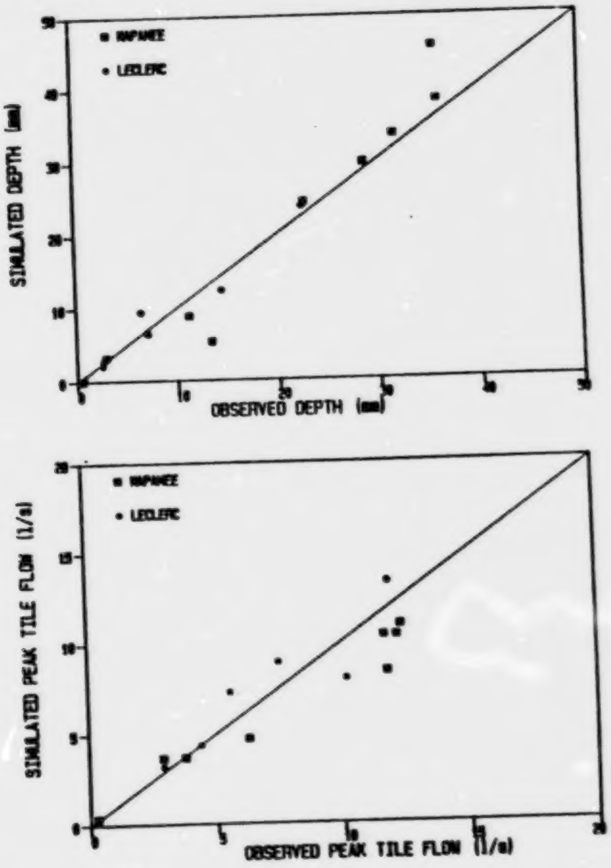


Figure 7 Observed and simulated depths and peak flows

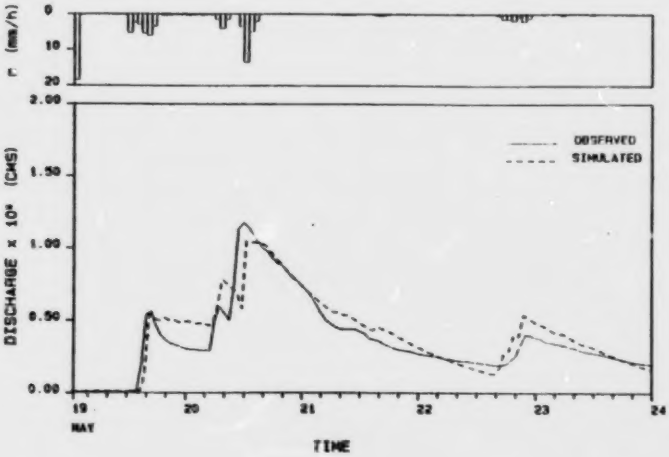


Figure 8 Observed and simulated hydrographs - Napanee Field

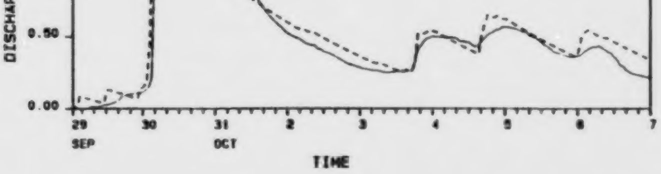


Figure 9 Observed and simulated hydrographs - Leclerc Field

require modifications. Figures 8 and 9 display the modelled and observed tile flows for a selected event for each field. Field characteristics and calibration values of parameters are given in Table 4.

Table 4 Field characteristics and parameters

Characteristic / Parameter	**Napanee Field**	**Leclerc Field**
Tile Spacing (m)	12.2	16.8
Depth upper layer (mm)	300	300
Depth lower layer (mm)	700	700
Area (ha)	5.7	14.0
Hydraulic conductivity K_s (m/d)	0.3	1.0
Depression storage L	0.02	0.10
Drainable porosity D (mm)	2	10
Ultimate infiltration f_c (mm/h) capacity	12	40
Depth to impervious layer from tile axis (m)	1.5	0.85
Field capacity upper layer	0.25	0.17
Field capacity lower layer	0.45	0.17

Model Sensitivity

In addition to the calibration and verification exercises, the model was subjected to tests to ensure that the sensitivity of the model to reasonable changes in parameters was compatible with the sensitivity of the real system to the same changes. Table 5 displays the parameters in order of their influence on tile flows for realistic changes in their values, the range over which the parameter was varied, and the range of the peak discharges and volumes in comparison to the final calibration run.

Table 5 Sensitivity of tile model to parameter changes

Parameter	Range	Q_p as percentage of calibrated value	Volume as percentage of calibrated value
Initial soil moisture content	±30%	40 - 140	45 - 160
K_s	x 2 & x 1/2	40 - 190	70 - 120
μ	±25%	80 - 140	90 - 115
Depth to impervious layer	±0.5 m	75 - 115	90 - 104
Depth upper layer	±100 mm	98 - 105	90 - 110
f_c	x 3 & x 1/3	80 - 100	85 - 100

Estimation of Parameters and Model Applications

Because of the relatively few parameters required and because of their physical basis, the model should be relatively easy to apply to uninstrumented fields for purposes of the design or assessment of tile drainage systems. Table 6 identifies the key model parameters and suggests a method for their estimation for uninstrumented fields.

Table 6 Estimation of model parameters

Parameter	Typical Range	Method of Estimation
Diameter of tiles	50 - 250 mm	Measurement
Spacing of laterals	5 - 20 m	Measurement
Slope of field	0.001 - 0.1 m/m	Measurement and calculation
Hydraulic conductivity	0.01 - 10 m/d	Auger hole method or Guelph permeameter or typical literature values
Depth to impervious layer	0.5 - 5 m	Measurement, or soil maps
Drainable porosity	1 - 15%	Literature values
Depression storage	2.0 - 25 mm	Literature values and qualitative assessment
Initial moisture content	0.05 - 1.0	Field capacity for design purposes (literature values)
Depth of upper layer	0 - 300 mm	Measurement
Vegetation parameter in Holtan's equation	0.1 - 1.0	Literature values
Ultimate infiltration capacity	0.5 - 100 mm/h	same as K_s

Seasonal Impacts of Tile Drainage on Fields

Because the hydrologic response of an agricultural field, whether tiled or not, is heavily influenced by antecedent moisture conditions, it is impossible to assess drainage impacts on peak or low flows through the examination of single events. Antecedent moisture conditions are a function of the drainage intensity and the prevailing climate (temperature and rainfall) prior to the event of record. In order to assess quantitively the impacts of tile drainage on peak and low flows, it is necessary to examine the hydrologic response of tiled and otherwise physically identical untiled fields over a season.

To determine these impacts as realistically as possible, the seasonally calibrated runs for the Napanee and Leclerc fields were used to define the hydrologic response of a drained field with respect to peak flows and low flows entering receiving water bodies. Because identical untiled fields have not been monitored, if in fact they exist, the model has been used to simulate these fields in an undrained condition for the same meteorological input. This undrained condition has been simulated by assuming ditch drainage along the field boundaries, resulting in an effective ditch spacing for the Napanee field of 100 m and for the Leclerc field of 90 m.

Results indicated that for the monthly hydrologic response the modelled evapotranspiration is very similar for both the tiled and untiled situations. As a result the total runoff volumes for both cases are similar (Tables 7 and 8). The key difference between the tiled and untiled cases is the shift between surface runoff and subsurface runoff. For the untiled case, the limited capacity of the ditches to remove subsurface flow rapidly forces the water table to the surface where excess water is removed via surface flow.

Table 7 Napanee field - Monthly hydrologic response for tiled and and untiled field - 1986

	TILED FIELD			UNTILED FIELD		
	Surface Runoff mm	Subsurface Runoff mm	Evapotranspiration mm	Surface Runoff mm	Subsurface Runoff mm	Evapotranspiration mm
April	0	21.6	24.2	0	5.1	24.2
May	18.2	45.6	43.8	52.7	8.8	43.8
June	3.6	40.3	51.0	37.2	9.3	51.0
July	0	0	73.3	0	6.4	73.3
Aug	4.2	10.2	67.0	4.6	6.6	67.0
Sept	21.7	88.7	36.4	95.5	10.5	36.4
Oct	0	55.3	21.2	35.3	12.2	21.2

Table 8 LeClerc field - Monthly hydrologic response for tiled and untiled field - 1986

	TILED FIELD			UNTILED FIELD		
	Surface Runoff mm	Subsurface Runoff mm	Evapotranspiration mm	Surface Runoff mm	Subsurface Runoff mm	Evapotranspiration mm
May	0	16.0	36.0	0	2.2	36.0
June	0	.3	57.4	0	5.2	57.4
July	0	14.6	64.5	0	7.8	70.7
Aug	0	0	44.6	0	1.5	52.2
Sept	0	21.6	37.7	0	4.9	37.7
Oct	0	62.4	18.8	18.8	21.9	18.8

The seasonal effects of tile drainage have been assessed using flow duration data for the 1986 season as illustrated in Figures 10 and 11.

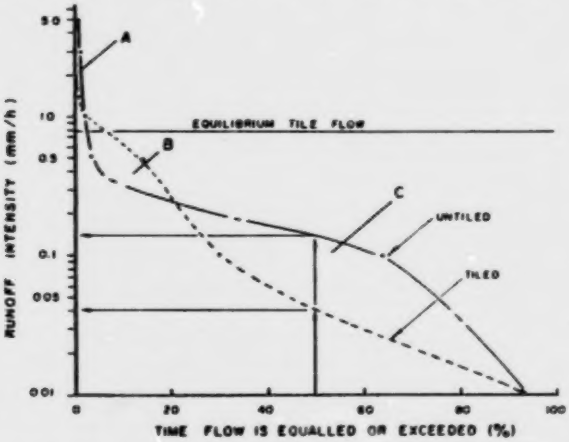


Figure 10 Flow duration curves Napanee field 1986 season or tiled and untiled cases

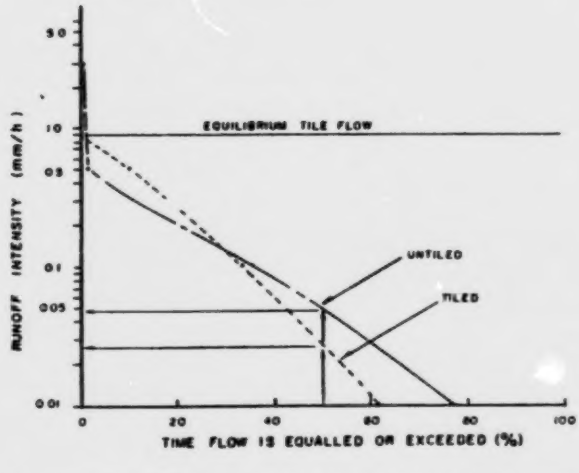


Figure 11 Flow duration curves Leclerc field 1986 season for tiled and untiled cases

Using the Napanee flow duration curve as an example (Figure 10), for 50 percent of the time, runoff intensity in the tiled field would equal or exceed 0.04 mm/h. The runoff intensity for the undrained case would equal or exceed 0.14 mm/h, 50 percent of the time. The impacts of tile drainage on the Napanee field are well illustrated by the flow duration curve, which can be divided into three distinct areas. Area C illustrates the effect tile drainage has on the low flows. An efficient tile drainage system removes the excess moisture storage in the soil profile quickly whereas an untiled field will provide a longer sustained interflow. The result is that the low flow periods will be increased when a field is tiled. Area B illustrates that for a smaller period of time and for intermediate flows below the equilibrium tile flow, a tiled field will experience higher flows. This expresses the increased efficiency of the tiled system for removing moderate amounts of excess rainfall rapidly. Rainfalls of an intensity up to the equilibrium tile flow can be removed without surface runoff from a tiled field. Finally, for a very small portion of time (Area A) and for flows in excess of the maximum tile drainage rate, it can be seen that high flows from the untiled field exceed those from the tiled field. This is a result of high intensity rainfalls which occur on saturated soil, thus producing surface runoff. As the soil profile is generally saturated or wetter for a longer period of time in the untiled field, which can only release water slowly through evaporation or interflow, any heavy rainfalls are more likely to produce surface runoff. A similar distribution of flows occurs for the South Nation test field when modelled in a tiled and untiled state (Figure 11), although the differences are smaller, likely as a result of the relatively pervious nature of the sandy soil in its natural state. In summary, for both fields, tiling has the effect of decreasing the number of high flows and increasing the duration of drought (very low) flows.

Both the number of events with surface runoff and the incidence of water tables in the root zone are increased for the untiled situations. This is particularly evident in the clay soil of the Napanee field. Excess water in the root zone (upper 30 cm) is expressed as cumulated cm-days for each month in Table 9. Skaggs (1978) indicates that although this index (denoted SEW_{30}) is a crude index, it nevertheless is a convenient method of approximating the quality of drainage. In general, values during the growing season greater than 100-200 cm-days can be expected to decrease crop yields.

Table 9 Excess water in root zone (cm-days) 1986 simulation

	Napanee Field		Leclerc Field	
Month	Tiled	Untiled	Tiled	Untiled
April	0	151		
May	24	216	0	0
June	10	205	0	0
July	0	0	0	0
Aug	0	0	0	0
Sept	51	488	0	5
Oct	0	678	0	646

Impacts at the Small Basin Level

Following the development and calibration of the tiled field simulation model, the model was extended to permit the simulation of a small agricultural basin. Channel routing algorithms for field ditches and main drains were developed to route and add flow from individual tiled or untiled fields. The output from the small basin model reflected the effects of channel lags on the hydrograph at the outlet of the small basin.

Impacts of drainage at the small basin level were assessed by the modelling of a small agricultural basin on Wilton Creek (Figure 12), approximately 5 km from the gauged Napanee field. The subbasin consists of sixteen fields ranging in size from 3 to 20 ha for a total drainage of 168 ha. Two soil types predominate in the basin: Napanee clay and Bondhead sandy loam. Corn, hay and soybeans are the principal crops. Nine fields with a total area of 74 ha (44 percent of total area) are presently tile drained. The watershed has been improved by ditching to link the fields into an efficient drainage network. Individual field elements are modelled using the field model as a subroutine. Field elements are added and hydrographs lagged appropriately to accommodate travel times in the channels. With the meteorological data from the summer of 1986, three physical situations were appraised for the subbasin. These were the existing level of drainage, the basin with no tile drainage, and a maximum level of tile drainage.

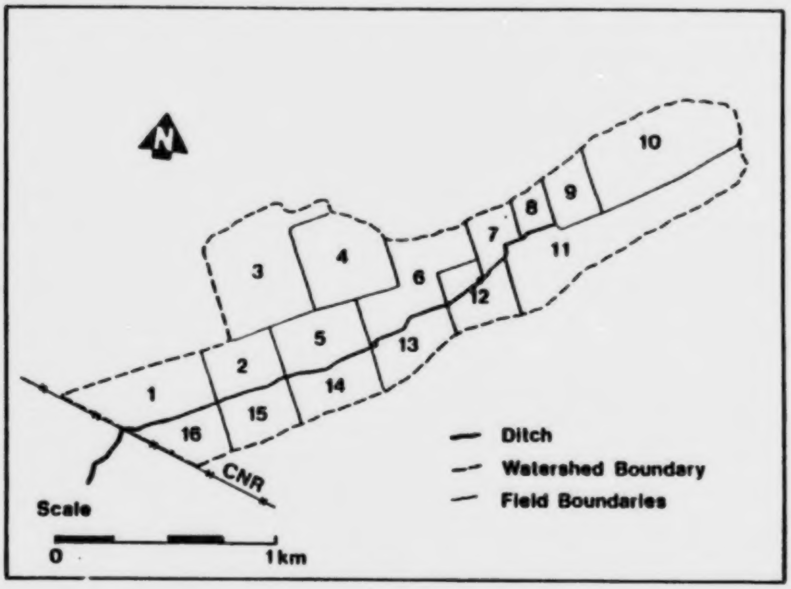


Figure 12 The Wilton Creek subbasin

Peak Flows

The effect of the alterations on modelled peak flows is displayed in Table 10 for the eight largest events in the season. Also noted in this table are the peaks with the channel lags removed. In every instance increasing the area tiled reduces the peak flows at the basin outlet, with a reduction in flow peaks of up to 80 percent for the maximum tiled case over the untiled situation. Removing the channel lags has very little effect on the peak flows, indicating that changes at the field level provide greater impacts than improvements to the efficiency of the ditch network. Ditches in other areas of Ontario, where substantial storage exists in the ditch network, may provide more significant impacts than in the Napanee area where ditch storage is negligible.

Table 10   Small basin model results - peak flows

Event	No tiles (m^3/s)	Existing drainage (m^3/s)	Maximum Drainage (m^3/s)
May 20	1.90 (1.93)	1.90 (1.99)	1.42 (1.57)
June 12	1.54 (1.88)	1.21 (1.542)	.49 (.48)
August 8	.41 (.47)	.36 (.45)	.24 (.38)
Sept 11	2.62 (2.48)	1.99 (1.89)	.74 (.74)
Sept 15	.58 (.57)	.43 (.41)	.12 (.12)
Sept 23	2.10 (2.13)	1.45 (1.40)	.42 (.51)
Sept 30	0.92 (.75)	.66 (.70)	.23 (.23)
Oct 14	.60 (.60)	.43 (.42)	.14 (.14)

* Figures in brackets represent the output with no consideration of channel lag times

Figure 13 illustrates the storm of September 11, 1986 (90.4 mm of rainfall) for the three levels of tile drainage modelled. It is noted that the maximum tile drainage situation attenuates the peak outflow of the subbasin by over 80 percent. Also shown on the figure for comparison is the discharge level from the subbasin which would be compatible with a typical drainage coefficient of 18 mm /day (0.75 mm/h).

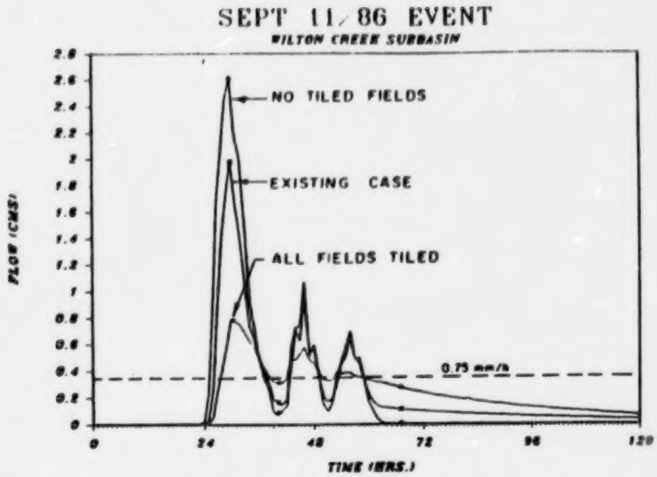


Figure 13 The effect of various levels of tile drainage on the basin response to a rainfall event

Low Flows

Although peak flows are attenuated with tile drainage, which may provide some flood relief to receiving water bodies, low flows are aggravated. Average flows during the month of July are 0.00053 m^3/s, 0.00098 m^3/s and 0.0 m^3/s for the untiled case, the existing case and the maximum tiled situation respectively. The existing situation, with 40 percent of the area tiled, has low flows in the order of 50 percent of that which would occur with no tiles, while the maximum possible tiled case has no flow during the month of July.

SUMMARY AND RECOMMENDATIONS

A model capable of reproducing the hydrological processes of a tile drained field has been developed, calibrated and verified on two fields in southern Ontario. The model, which is capable of running in a continuous mode on a personal computer, possesses physically-based parameters which for the most part can be relatively easily determined independent of the model itself. The overall performance of the model with respect to reproducing flow peaks, volumes and hydrograph shapes is excellent.

The model, in its continuous mode, was used to assess the impacts of tile drainage systems on peak and low flows at the field level and at the small basin level. Application of the model to the test fields and the statistical examination of meteorological data and streamflow data led to the following conclusions regarding the impacts of agricultural drainage in Ontario.

- Statistically significant evidence of the impact of tile or ditch drainage on streamflows is extremely difficult to obtain. An examination of flow records for trend indicates that alterations to the flow series as a result of climatological trends far overshadows any lesser trends resulting fromactivity.

- The hydrologic response of a tile drained field is particularly sensitive to antecedent moisture conditions prior to rainfall events. Because the tile drained system affects the soil water balance and hence the antecedent conditions in a field, it is impossible to comment on the impacts of tile drainage through an examination of independent rainfall events. It is necessary to consider seasonal periods to establish the changes in the frequency of various surface or subsurface hydrograph peaks and volumes.

- A simple deterministic hydrologic model can, when calibrated, be used successfully to assess the impacts of tile drainage on peak and low flows for various field characteristics and soil types.

- Tile drainage in southeastern Ontario does affect peak and low flows. In general, draining exacerbates low flow periods during summer months (July and August) and reduces the frequency of high flows as a result of intense rainfall events.

- Tile drainage does not significantly change the total volume of runoff, but the relative magnitudes of surface and subsurface runoff are significantly changed. The subsurface flow, which would be interflow in the untiled case and largely tile flow in the tiled case, is increased significantly for tiled fields. Because of this alteration in flow paths to receiving streams, it is expected that other processes requiring water as a transport medium will be altered significantly. These processes could include soil erosion, nutrient runoff, and herbicide and insecticide transport and decay mechanisms.

It is recommended that:

- to extend the use of the model to other areas of Ontario, efforts should be concentrated on relating the required model parameters to published (readily available) information on soil types and land use;
- the model be linked to water quality algorithms to assess the impacts of drainage activity on water quality in receiving streams;
- additional work be performed, including calibration and verification at the small basin level to test the robustness of the model when integrating several agricultural fields (both tiled and untiled, and crop and pasture land uses); and
- the model and other information be disseminated to other government agencies as it becomes available with a view to ultimately applying the information in a practical manner for land use assessment or tile drainage design.

ACKNOWLEDGEMENTS

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An Expert System
for Water Quality Assessment

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L. Logan (2)

Abstract

WatQUAS – a prototype expert system has been developed to interpret historical water quality data. The expert system mimics a human hydrological expert in judging the statistical analysis of a time series representation of water quality at a site. The system incorporates standard statistical analysis techniques and knowledge engineering methods in interpreting the data based on hydrological heuristics compiled in a knowledge base.

Introduction

Computers have been used traditionally as fast numerical calculating machines and are indispensible tools of modern society's information processing trend. However, human insight, creativity, and flexibility still predominate in even the most simple problem-solving tasks. But with the advent of artificial intelligence (AI) came the product Expert Systems – computer programs which mimic human expertise in some limited particular domain. Today expert systems enjoy wide-spread use in a variety of fields such as medical diagnosis, oil exploration, or emergency spill procedures.

Expert system applications avoid many of the pitfalls of traditional computer software packages. Typical computer algorithms rely on 'black-box' approaches to problem-solving. This approach works well for well-defined numerical problems but is woefully inadequate for problems requiring judgement or having incomplete data. Expert systems are a type of Knowledge Based System – a system which relies on machine 'understanding' of problems rather than rigid mathematical algorithms. For this reason, expert systems are often designed to accommodate symbolic information and making conclusions regarding the *meaning* of the data.

Hydrological engineering problems often involve processing large amounts of sampled measurements (time series). Most hydrological data processing incorporates many such 'black-box' models and thus suffers many the limitations inherent in the models. With regard to stochastic time series models, [Unny, 1981] states:

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> "It should be emphasized here that this procedure bears no relationship to the physical phenomena on which the data has been recorded. In addition, this procedure could often become irrelevant when its results are applied in connection with water resources planning and management. Objections can also be raised from heuristic and philosophic points of view. All that is required to complete the above procedure [time series modeling] is a few parameters -- at the most three or four — determined from the data; otherwise the whole set of data so laboriously collected can be discarded."

These limitations do not imply that such models are useless; they only demonstrate the extent to which the results can be justifiably used in engineering judgement.

Water quality assessment as a branch of hydrology incorporates both deterministic facts such as concentration measurements and quantifiable geographical situations with the more obscure concepts of environmental risk assessment and socio-economics. Part of the water quality expert's task is to pass judgement on data and attach symbolic meanings to the data. The interpretive procedure is ill-defined and resists conventional modeling methods. In fact, hydrologists quite often differ among themselves as to what knowledge is relevant and how to define the interpretive procedure. This ambiguous nature of water quality assessment makes it an excellent candidate for an expert system application.

Water Quality Assessment as an Application

Not all domains are good candidates for expert system application. The domain should depend a great deal on symbolic reasoning and should contain obscure or ambiguous qualities of a type difficult to model numerically. Water quality assessment is a good candidate because assessment experts are often involved in data *interpretation* (symbolic processing) and the process of interpretation is still ambiguous.

Often, water quality experts must assess the seriousness of an identified problem and prescribe remedial abatement strategies taking into account socio-economic factors, the chemical nature of the pollutant (environmental impact) and other features such as data uncertainty and statistical trends. The complexity of the ecosystem coupled with the many unknowns of today's myriad of chemical pollutants combine to create a very obscure problem.

Data used in water quality assessment often takes the form of sets of time series for several pollutant concentrations at selected sites. In Ontario, measurements of selected water quality parameters are taken at regular intervals and are compiled to form a historical data base for that site. For economic and practical reasons, not every parameter is measured at every site, but rather parameters deemed important for a particular station are measured and used as a metric for that area's water quality. Major parameters are total and fecal coliforms, biological oxygen demand (BOD$_5$, phosphorous, phosphates, acidity, nitrates, suspended solids, turbidity, pH, and the concentrations of metals and select elements or compounds. The Ontario Ministry of the Environment has published its policy on water quality and defines acceptable levels or some classes of pollutants.

Fortunately, not every aspect of water quality assessment is shrouded in uncertainty. Years of research have discovered important relationships and repeating phenomena. For example, laboratory tests can determine lethal concentrations of certain compounds. But the ambiguities outweigh deterministic knowledge by far. Uncertainties arise due (not exclusively) from four causes:

- biological complexity
- weakness inherent in testing
- uncertain sources
- interaction of water quality, acquatic life, and socioeconomic concerns (synergy of ecosystems)

WatQUAS

WatQUAS addresses this issue of ambiguity in data interpretation. In planning WatQUAS as an assessment tool, the following *general* goals were put forward:

- to provide a user-friendly interface to water quality data
- to interpret historical water quality data in a expert fashion
- to function as a tool in planning based on expert water quality assessment

As a computer application, the following objectives were stipulated:

- user-friendliness
- modularity
- flexibility
- robustness

Lastly, as an expert system, the following objectives were itemized:

- easy to use
- educational when appropriate
- able to explain advice and rationale
- able to respond to simple questions
- able to learn new knowledge
- easily modified

In constructing WatQUAS, the basic premise as suggested in [Sell, 1985] was considered:

> "to make a program intelligent, provide it with lots of high quality, specific knowledge about some problem area."

Many of the concepts and definitions discussed in [Hayes-Roth, 1983] were used in WatQUAS' development.

Computer Resources

WatQUAS 1.0 was developed at the University of Waterloo on a VAX 11/785 networked via ethernet with a VAXstation II/GPX. Both machines ran the UNIX 4.2bsd operating system. The VAXstation II/GPX is a MicroVAX machine with dedicated colour bitmapped graphics hardware and was used for graphics representation of statistical information. The statistical and user interface components of the system were writting in the C programming language and the expert system modules were written in OPS83 - a production-rule language specially designed for expert system applications.

System Strategy

Following the goals and guidelines descibed above, a system as diagrammed in Figure 1 was constructed to meet the objectives. WatQUAS was constructed as a command-driven software package. Commands typed at a terminal are parsed and submitted to a command-processor. The novel aspect of WatQUAS lay in its use of an expert system interpreter. The statistical analysis modules perform standard arithmetic operations on the raw data (files of water quality measurements indexed by time) to produce a statistical summary of the data.

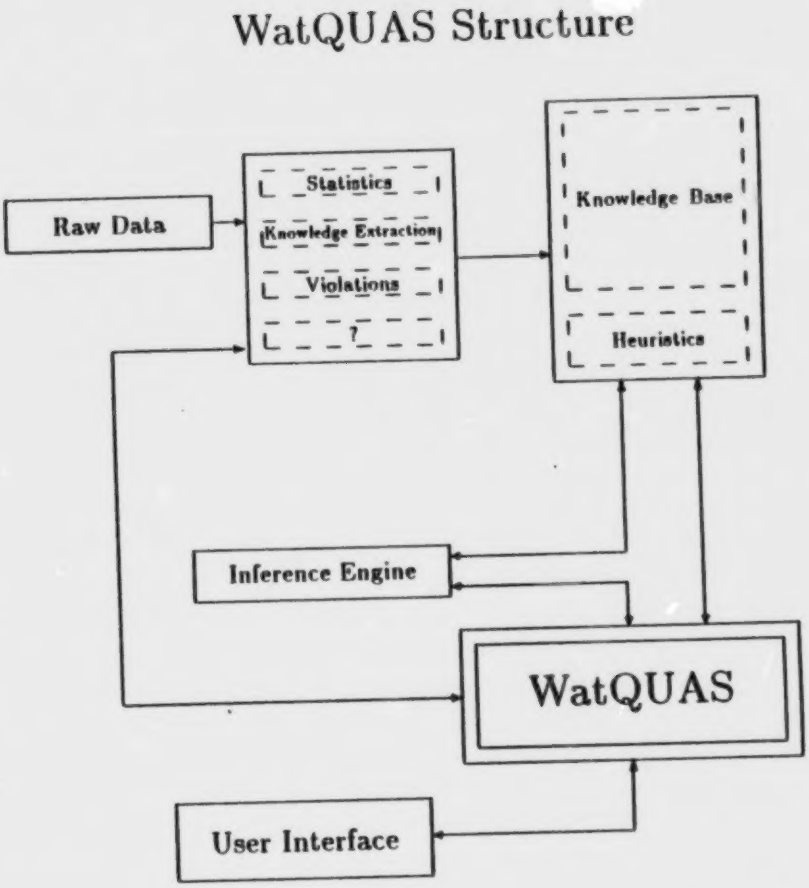
WatQUAS Structure
Raw Data
Statistics
Knowledge Extraction
Violations
?
Knowledge Base
Heuristics
Inference Engine
WatQUAS
User Interface

Figure 1 WatQUAS Structure

Other modules compute the statistics of threshold violations using to lookup tables. Another module computes a modified composite water quality index based on a Delphi technique described in [Canter, 1985]. So far, this represents only conventional programming technique.

To *interpret* these extracted data, the user types an appropriate command and a separate module is invoked to assess these data according to rules (heuristics) compiled in the Knowledge Base. This knowledge base coupled with the inference engine composes the expert system component of WatQUAS.

Heuristics in the knowledge base are of four types and are discussed briefly:

Assessment Rules

These rules implement an interpretive procedure described in [Canter,1985] namely:

- establish water quality at a site (eg. water quality index)
- analyse data for trends
- identify parameter relationships and significance
- assess sampling practice adequacy
- compute environmental risk and make recommendations if necessary

Other assessment rules interpret the statistics by assigning a seriousness to situationsan compute a symbolic overall seriousness based on violation trends, toxicities, and statistical trends in the time history.

Parameter-specific Rules

These heuristic deal with the unique properties of individual chemicals. Such individual features dictate the importance of toxicity, environmental impact, and health risk implications of a particular substance. An example of this type of heuretic may be stated:

Rule: Fecal Coliform environmental Risk
If: the fecal coliform levels at a site are not satisfactory
and the site being considered uses water for drinking or recreation
Then: the health risk at this site is substantial

Other parameter rules deal with the issue of missing information. If only partial information is known about the presence of a substance, an expert may wish to know something not found in the data. Such a rule would recognize the lacking information and prompt the user for it and know how to procede with or without appropriate user response.

Hydrologic Rules

These rules consider the geographical and station characteristics in assessing data. For example, streamflow or station classification may influence the importance given to certain parameters. An example of the geographical-type hydrological rule is stated:

Rule: Agricultural Site Parameter
If: the site is designated as an agricultural monitoring site
or the site is in an agricultural setting
Then: the following parameters are important (ones to watch):
fecal coliforms, any pesticide, any nutrient parameter

Socio-economic Rules

Risk assessment and abatement strategy knowledge is embodied in the socio-economic rules. Demographic detail used in strategy making and identifying likely pollutant sources are some of the issues addressed by these heuristics. An example of this rule type is:

Rule: High risk urban sites
If: site is urban
and human health related parameters have been found with serious violations
Then many people are at risk
and abatement strategies should be implemented (strong recommendation)

Other rules would specify the abatement strategy based on which parameters were found to be present in high quantity.

These rules are represented as *patterns* in the knowledge base and the inference engine uses a conflict resolution strategy described in [Forgey, 1985] to match data patterns with appropriate rules. This processing continues until a non-processable state is reached at which time a signal is sent to the user interface (keyboard plus screen) indicating that processing is complete. A report in human-readable format is generated summarising the result of the interpretation. *Qualitative* as well as quantitative assessments of the data are provided. For example, such words as *serious, good, bad, potentially dangerous* (all words indicating a judgement call) are attached to a numerical description of a site.

Other features of WatQUAS include the graphical representation of trends and parameter histories on the VAXstation II/GPX. This feature provides the user with a *picture* of the data.

Conclusions

WatQUAS has significant potential as a usable tool in the hands of both hydrological engineers and non-experts. The integrity of a final version will depend largely on the size and quality of the heuristics assembled in the knowledge base. Other knowledge extraction techinques can be incorporated into its modular structure to provide more data to aid the interpretive process. Development of the system may incorporate natural language processing and regional planning and assessment strategies.

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PILOT SCALE STUDIES OF THE REMOVAL OF TRACE ORGANIC CONTAMINANTS FROM DRINKING WATER BY CONVENTIONAL PROCESSES

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INTRODUCTION

The presence of trace concentrations of synthetic organic chemicals (SOCs) in finished drinking water supplies is of concern for numerous reasons, not the least of which is the possibility of health effects on consumers. As a result, considerable effort has been undertaken to re-evaluate conventional treatment methods, as well as alternate technologies, for reducing the levels of SOCs found in drinking water. This project has been undertaken to determine the effectiveness of optimized conventional water treatment processes and conventional treatment followed by granular activated carbon adsorption (GAC) for the removal of trace levels of SOCs. The bench and pilot scale tests that have been conducted for the conventional treatment process evaluation are discussed here.

A preliminary phase of groundwork was completed before the actual pilot plant experiments to evaluate the removal of SOCs were conducted. This included the selection of a group of SOCs for monitoring and spiking purposes, the development of analytical methodologies for those specific compounds, and the design and construction of a pilot scale drinking water plant.

The 34 monitoring compounds were chosen from an initial listing of over 300 organic chemicals found in the Niagara River. The decision tree used in establishing the monitoring list ensured that compounds from 11 different chemical classes, with wide ranging chemical and physical properties, were chosen. Other parameters considered in establishing this list included the environmental levels of the chemicals, hazard and toxicity ratings, as well as the aquatic and drinking water criteria of several jurisdictions.

Analytical methodologies were required for the routine monitoring of the 34 target compounds. This work included the establishment of instrument and method detection limits for all of the target compounds, often at levels lower than those used in standard methods.

A new drinking water treatment pilot plant was designed, fabricated of chemically inert materials, and installed at Niagara Falls.The plant underwent complete initial testing during the preliminary work leading to the pilot plant experiments.

For the evaluation of the conventional treatment processes for removing SOCs, a sublist of chemicals was chosen from the list of 34 monitoring compounds for spiking into the pilot plant's raw water supply. The spiking program is necessary to ensure that a constant, known concentration of SOCs is maintained in the raw water. It is the removal of these spiked SOCs by the conventional treatment processes that is discussed here.

EXPERIMENTAL

Jar Testing

The goal of the jar testing program was to determine the best performing coagulant(s) for the removal of turbidity and natural organic matter, and establish the optimum coagulant dose and operating pH for that system. Dissolved organic carbon (DOC) and ultraviolet absorbance (UVA) at 254 nm were used as a measure of the organic carbon levels in the water. Turbidity, colour, pH and alkalinity measurements were made as well.

The three primary coagulants that were evaluated were alum, polyaluminum chloride (PACl), and ferric chloride. Both alum and PACl stock solutions used in the tests were obtained by diluting the commercial products, while ferric chloride was made up in the laboratory from the reagent grade chemical.

Each of the primary coagulants was tested using a matrix of concentration and pH combinations. The doses ranged from 1 to 16 mg/L for PACl and ferric chloride, and from 2 to 32 mg/L for alum. The pH range went from 5.0 to 7.5, in increments of 0.5, with the last test run at the ambient pH of around 8.3.

The primary coagulants were ranked according to their performance in removing turbidity, DOC, and UVA, as well as the cost to produce a given volume of water at the optimum pH and coagulant dose conditions.

A total of five secondary coagulants were evaluated. Activated silica and CatFloc B were evaluated with alum at a fixed dose. Three other polyelctrolytes (LT31, a long-chain cationic polymer; 6465, an anionic polymer, and LT20, a nonionic polymer) were tested with all three primary coagulants. The tests were conducted at the optimum dose and pH conditions already determined for each primary coagulant. The stock solutions for these chemicals were made up fresh in the laboratory prior to use.

The underlying philosophy of the evaluation of the secondary coagulants was to determine if they could improve the quality of the filtered waters compared to the use of the primary coagulants alone, at the same dose and pH conditions. The intent was to determine if the use of the secondary coagulants could reduce the amount of primary coagulant needed to produce the same quality water.

The initial tests were conducted in late summer, with warm ambient water temperatures. Some tests were subsequently carried out in an ice bath to maintain temperatures below 4°C, and simulate winter conditions. This gave an indication of the relative performance of the primary coagulants when used at low temperatures. The coagulants will be re-evaluated when the pilot plant is in operation during winter months.

The cost to produce the best quality water is also an important factor in the evaluation of the chemicals tested. If two coagulant systems are capable of producing a similar "best" quality of water, then the scheme with the lower cost would obviously be preferred. Therefore, the amount of coagulant(s) used and their unit prices, the amount of sludge produced and the cost of disposal, as well as the operating pH with the cost of pH ajustment chemicals, would all influence the choice of an optimum system.

Pilot Plant Evaluation of Jar Test Results

The pilot plant models a complete water treatment process consisting of flash mixing and coagulation, flocculation, sedimentation and filtration. The materials of construction as well as all process equipment and instrumentation were carefully selected so that all water-contacting surfaces throughout the entire delivery and treatment processes are of chemically inert substances (i.e. glass, teflon, and stainless steel).

Raw water from the Niagara River is supplied to the pilot plant via a dedicated pump which draws from the Niagara Falls WTP intake system. The coagulants and pH adjustment chemicals are delivered by duplexed low flow metering pumps from calibrated storage vessels and injected into the raw water. Flash mixing for these chemicals is done with an 8 stage Komax-type static mixer. The flocculator is designed for a 3.8 L/min (1 USgpm) flow, and has three compartments with hydraulic detention times of 10 minutes each. Sedimentation occurs in a Lamella-type plate clarifier, with an overflow rate of 4.75 m/hr. The filter is a 10.2 cm diameter glass column, and operates at a flowrate of 12.2 m/hr (5 USgpm/ft^2). A built-in plenum supports 24.5 cm of sand and 43 cm of anthracite, taken from filters in service at the Niagara Falls plant.

A conceptual drawing of the pilot plant's conventional process treatment train is shown in Figure 1.

The two best coagulant systems selected from the jar testing program were further evaluated in the dynamic conditions of the pilot plant. As per the jar tests, a matrix of dose and pH combinations was used to evaluate the coagulants. The pH and coagulant dose ranges tested bracketed the optimum values determined in the bench tests. Cost to produce the best quality water was also evaluated. The coagulant and operating conditions that gave the best water quality were then chosen for use during the subsequent pilot plant evaluations of the removal of the spiking SOCs.

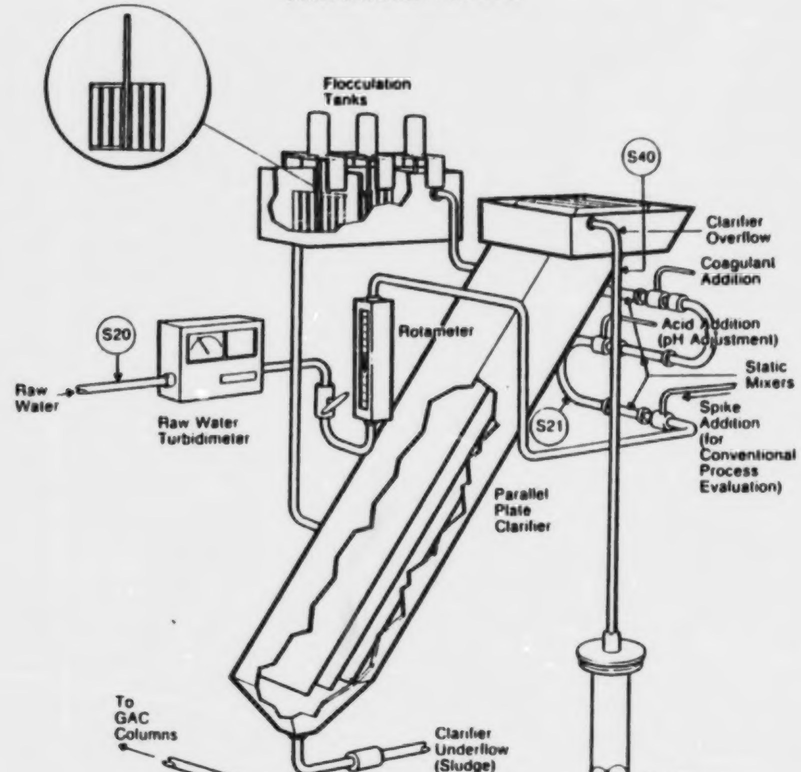
Each coagulant was evaluated in the pilot plant over a period of several days, after allowing the pilot plant to come to steady-state conditions. This involved selecting the correct energy input and gradient to the flocculation chambers, establishing a sludge blanket in the plate settler, and determining the proper underflow from the sludge hopper.

Pilot Plant Evaluation of Conventional Treatment Process for the Removal of Spiking Chemicals

Based on the selection of the targeted 34 monitor compounds, 13 spiking compounds were chosen for these experiments. These SOCs represent a wide range of physico-chemical characteristics relevant to water treatment operations. In other words, the selected chemicals possess properties that might establish the limits of the conventional and GAC treatment processes.

FIGURE 1

Niagara Falls Trace Organics Project
Pilot Treatment Plant
Conventional Process


Flocculation Tanks
S40
Clarifier Overflow
Coagulant Addition
Acid Addition (pH Adjustment)
Static Mixers
Spike Addition (for Conventional Process Evaluation)
S20
Raw Water
Raw Water Turbidimeter
Rotameter
S21
Parallel Plate Clarifier
To GAC Columns
Clarifier Underflow (Sludge)
Dual Media Filter
Rotameter
Filtered Water Turbidimeter
S50
S Sampling Location

These chemicals are:

- 1,2-Dichloroethane
- p,p'-DDT
- Tetrachloroethylene
- gamma-BHC
- Benzene
- Anthracene
- Chlorobenzene
- Pyrene
- 1,4-Dichlorobenzene
- Naphthalene
- 2,4,6-Trichlorophenol
- Hexane
- Decachlorobiphenyl

Due to the low solubility of some of the more hydrophobic compounds of interest, the feed solution of the spiking compounds was made up in acetone. With acetone present in large quantities as the solvent, analysis of the volatile compounds was not possible. Thus, results for 1,2-dichloroethane, tetrachloroethylene, benzene, chlorobenzene, 1,4-dichlorobenzene and hexane are not available for this phase of the study.

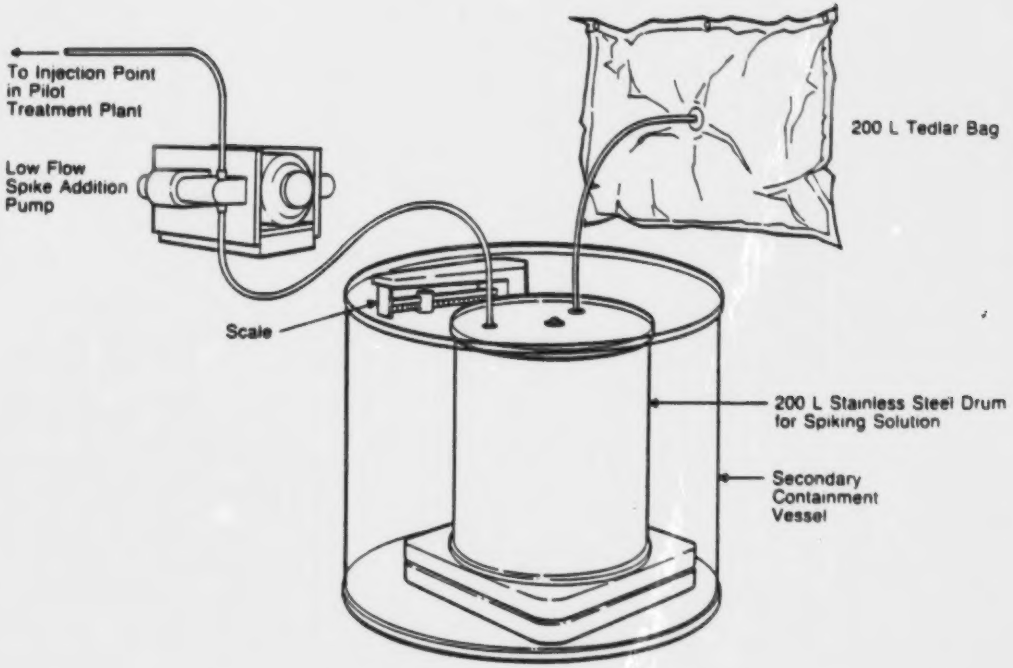
The spiking feed solution is delivered to the pilot plant by a duplex metering pump, and is injected into the raw water. The flash mixing of the spiking solution and the raw water is accomplished by a static mixer, ahead of the addition point of any treatment chemicals. The spiking solution is fed such a rate as to give a raw water concentration of the spiked SOCs of approximately 10 ug/L.

The spiking solution feed drum is situated within a secondary confinement drum, and sits on a weigh scale so that precise measurements of spiking solution feed rates can be made. A conceptual drawing of the spiking solution storage apparatus and delivery system is shown in Figure 2.

Two preliminary tests were conducted prior to the pilot plant evaluation of the removal of the spiking compounds. The first test determined the contribution of organic chemicals to the raw water by the pilot plant materials, and the loss of ambient SOCs onto pilot plant surfaces. The second test evaluated the loss of the spiking chemicals within the pilot plant.

There was no indication from the analysis of the first test that any of the pilot plant surfaces contributed to the presence of the DOC inherent in the raw water, or any SOCs. There was also no apparent loss of ambient level SOCs within the pilot plant.

The influent and effluent concentrations of some of the spiking chemicals showed significant variation during the second test. There are a number of possible factors contributing to this observation. There is a measurable, yet variable loss of the spiking compounds in the delivery to the pilot plant from the storage vessel, as well as some loss during injection into the raw water. Other factors could include adsorption of the spiking SOCs onto the pilot plant surfaces, volatilization from the open water surfaces, biological activity, and adsorption onto humic and particulate matter partially removed in the plant underflow.


To Injection Point
in Pilot
Treatment Plant
Low Flow
Spike Addition
Pump
Scale
200 L Tedlar Bag
200 L Stainless Steel Drum
for Spiking Solution
Secondary
Containment
Vessel

Niagara Falls Trace Organics Project
Pilot Treatment Plant
Apparatus for Storage and Addition of Spiking Compounds
FIGURE 2

It became evident that a quantitative measure of the removal of individual spiking compounds by any of the specific unit operations of the conventional treatment train could not be made. Instead, any measureable removal of the spiking compounds that was observed would have to be attributed to the conventional treatment process, regardless of whether this removal was a result of the treatment unit operations, adsorption onto water contacting surfaces, volatilization, and so on.

The pilot scale evaluation of conventional treatment processes for the removal of the spiking compounds began in May 1987. The pilot plant was operated for a period of two weeks, and sampling took place on the last six days of the run. Samples were taken of the spiked raw water influent, the settled water, and the filtered water. Duplicates of 33% of the samples were analysed. A second two week run was completed in September, 1987.

The pilot plant was operated under the following conditions. Polyaluminum chloride was used as the primary coagulant at a dosage of 8 mg/L. No secondary coagulant was used. The raw water was adjusted to a pH of 7.1 by addition of 2N nitric acid. Nitric acid was used rather than sulphuric acid in order to eliminate any impact of the sulphate ion in the coagulation process.

RESULTS AND DISCUSSION

Jar Tests

The following is a brief discussion summarizing the results of the more than 80 sets of jar tests performed in this phase of the study.

The Niagara Falls raw water used during the jar testing program was typically characterized by a turbidity of 1 - 2 NTU, DOC between 2 - 3 mg/L, colour of less than 5 ACU, pH in the range of 8.3 - 8.5, and alkalinity of approximately 100 (as mg/L $CaCO_3$).

In the tests using primary coagulants only, alum, ferric chloride and polyaluminum chloride had comparable performance when evaluated for their ability to remove turbidity, DOC, and UVA. Filtered water quality from these tests at optimum pH and dose conditions showed turbidities of below 0.1 NTU, DOC levels near 1.0 mg/L, and removals of total UVA of approximately 70 percent.

The optimum pH and dose operating zones for the three primary coagulants tested are compared in Figures 3, 4 and 5. These three diagrams outline the best removals by the primary coagulants of turbidity, DOC, and UVA respectively. The area above the plotted lines represents water quality at least as stringent as 0.1 NTU, 1.5 mg/L DOC, and removal of total UVA of greater than 60 percent, respectively.

FIGURE 3

Optimum Turbidity Removal (<0.1 NTU)

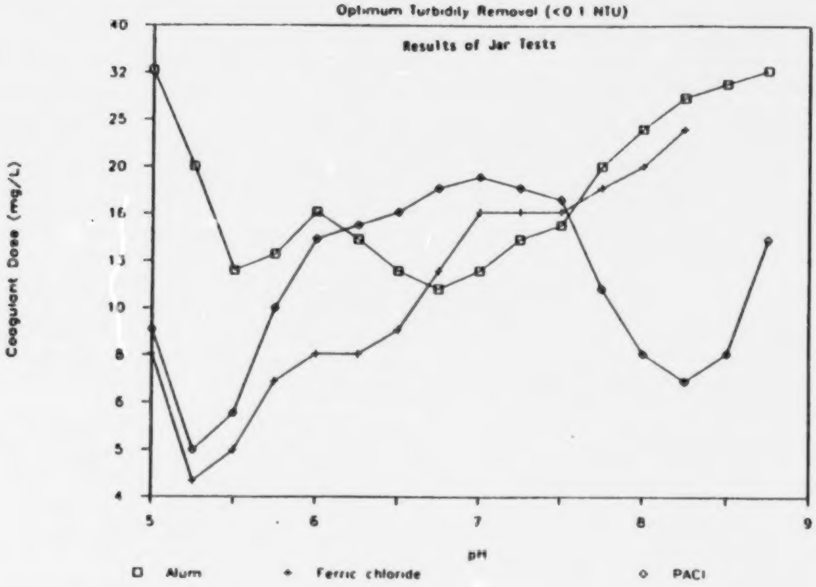
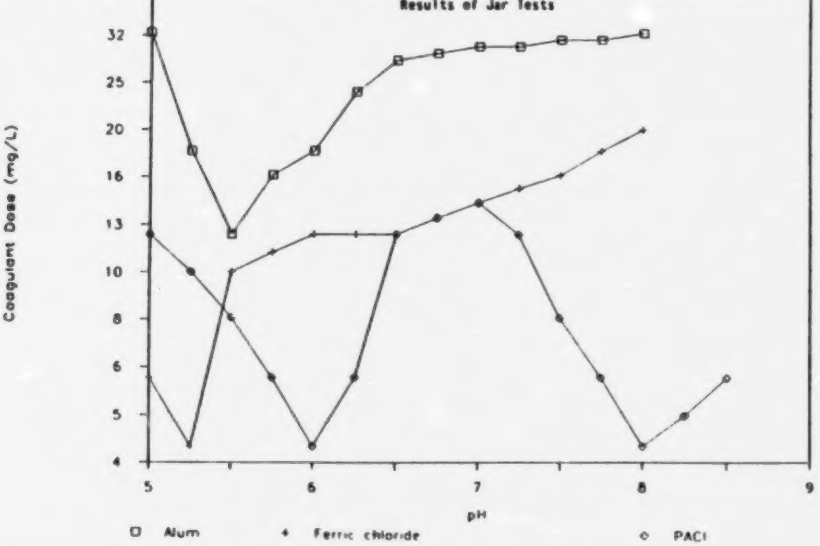


FIGURE 4

Optimum DOC Removal (< 1.50 mg/L)



The best filtered water produced by each coagulant had the following characteristics:

	TURBIDITY	DOC	% UVA REMOVAL
Alum	0.05 NTU	1.0 mg/L	69 %
Ferric	0.03	0.9	80
PACl	0.02	1.1	69

Although all three coagulants gave compareably good finished water quality, it is noted from these diagrams that the optimum pH and dose ranges are different for each. The table below summarizes the "safe" operating dose and pH requirements of each coagulant in order to meet the criteria of less than 0.1 NTU, 1.5 mg/L DOC, and greater than 60 percent UVA removal:

	TURBIDITY		DOC		UVA	
COAGULANT	mg/L	pH	mg/L	pH	mg/L	pH
Alum	12	6.5	16	5.5	16	6.0
Ferric	8	6.0	8	5.5	8	6.0
PACl	8	7.0	8	7.5	8	7.5

Less pH adjustment is needed for the use of PACl than for alum or ferric to achieve the best water quality. This holds true for the removal of all three of the parameters tested.

A cost comparison of the three primary coagulants was undertaken to determine the most economically viable coagulant system at the pH and dose conditions that resulted in the best water quality. Using suppliers prices for delivered chemicals, the costs outlined below are obtained.

	COAGULANT		pH ADJUSTMENT		
	mg/L	Cost	pH	Cost	TOTAL COST
Alum	12	2.60	6.0	9.33	11.93
Ferric	8	1.90	6.0	9.33	11.23
PACl	8	7.05	7.2	1.70	8.75

NOTE: All costs are in $/1000 m^3 of treated water.

his table shows that PACl has the lowest chemical costs per 1000 m^3 of water treated, followed by ferric chloride and alum.

It is noted that the significantly lower cost for pH adjustment for PACl is due its higher operating pH of 7.2. This is important for two reasons. First, the shape of the titration curve of alkalinity in Niagara Falls raw water between 7.0 and 6.0 requires that considerably more acid be added per unit pH increment in this range. Second, alum and ferric require initial pH adjustment to 6.0, and pH is further

FIGURE 5

Optimum UVA Removal (> 60 % removal)

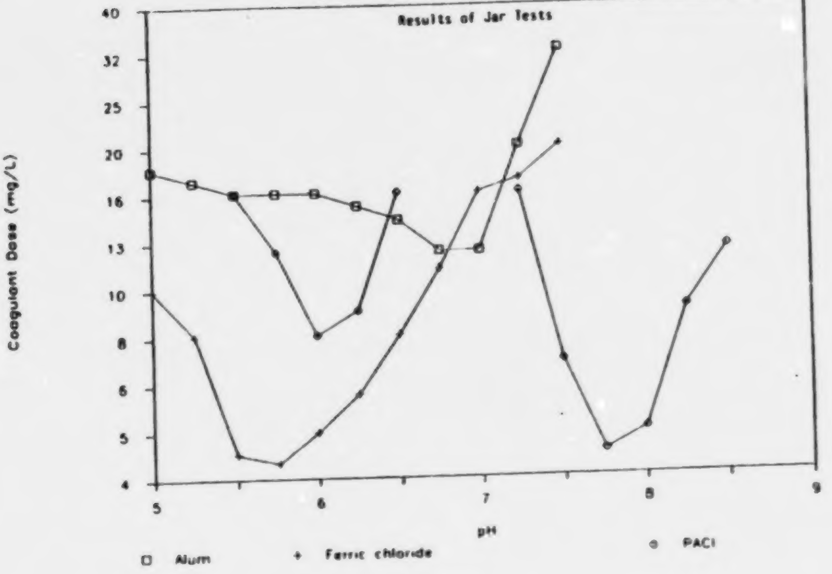
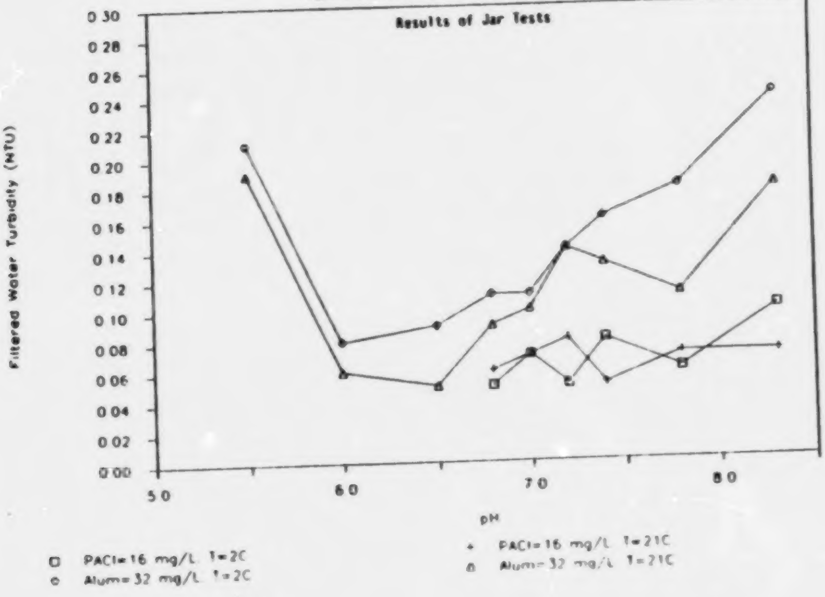


FIGURE 6

TEMPERATURE COMPARISON OF ALUM, PACl



lowered to approximately 5.6 after addition of the coagulants. It is therefore necessary to readjust the pH of the finished water back to a value of close to 6.5. This is not required for PACl when using an initial pH of 7.2, since the finished water has a pH of approximately 7.0.

Although the use of ferric chloride resulted in a finished water quality compareable to that of alum and PACl, the settled water had significantly higher turbidities at all pH and doses tested. This would affect the operation of the pilot plant, or a full scale plant, by resulting in shorter filter runs. It was also discovered that the UVA remaining in the settled water was much higher for ferric chloride than for either alum or PACl. In fact, the UVA removed in settled water samples for ferric chloride was less than 10 percent, compared to 50 to 60 percent for alum and PACl. If a plant were to be operated using the concept of multiple barriers, then the system that provided the greatest contaminant removal by all unit processes would be preferred. A system operated with ferric chloride as the coagulant would run the risk of having a significant breakthrough of DOC in the filter if a turbidity breakthrough occurred. This risk would be greatest when using ferric chloride, as most of the UVA is removed from the settled water delivered to the filter when either alum or PACl is employed.

The use of secondary coagulants did not enhance the performance of any of the primary coagulants. In some cases, particularly with PACl, the primary coagulant alone produced better filtered water quality than when used with a secondary agent. Of the polymers tested, the anionic polymer produced the best results with each of the primary coagulants, suggesting that there may have been a slight overdosing of coagulants in the other sytems. It should be remembered that the secondary coagulants were added in an attempt to see if a better water quality could be achieved at the optimum dose and pH conditions found for the primary coagulants alone. It was not undertaken to evaluate whether addition of the secondary agents would significantly lower the primary coagulant requirement and achieve the same water quality.

Alum and PACl were further evaluated at cold temperatures. Figure 6 shows that PACl outperforms alum for turbidity removal at higher pH values in cold waters as well as at warmer temperatures. The same general result is obtained when measuring UVA reduction, although there is an indication that PACl may achieve greater UVA removal at a pH near 7.0 than alum at any pH in cold water. Figure 6 also shows that the performance of PACl for particulate removal is affected very little by colder temperatures, if at all. These two coagulants will be further evaluated when the pilot plant is operated during winter months.

Based on the jar test results, it was decided to further evaluate the performance of alum and PACl in the pilot plant. No furhter tests would be conducted with ferric chloride or the secondary coagulants.

Plant Evaluation of Jar Test Results

In a manner similar to the jar test experiments, a matrix of pH and coagulant dosages was investigated. For PACl, dosages of 1 to 16 mg/L were used at a fixed pH of 7.2. Then, at a fixed dose of 8 mg/L, the pH was varied from 5.2 to 8.2. The raw water temperature during this testing was 14°C. For alum, a fixed pH of 6.2 was used to test doses of 8 to 28 mg/L. A dose of 16 mg/L was then maintained while pH was varied from 5.3 to 8.2. The raw water temperature during the alum evaluation was 20 C.

FIGURE 7

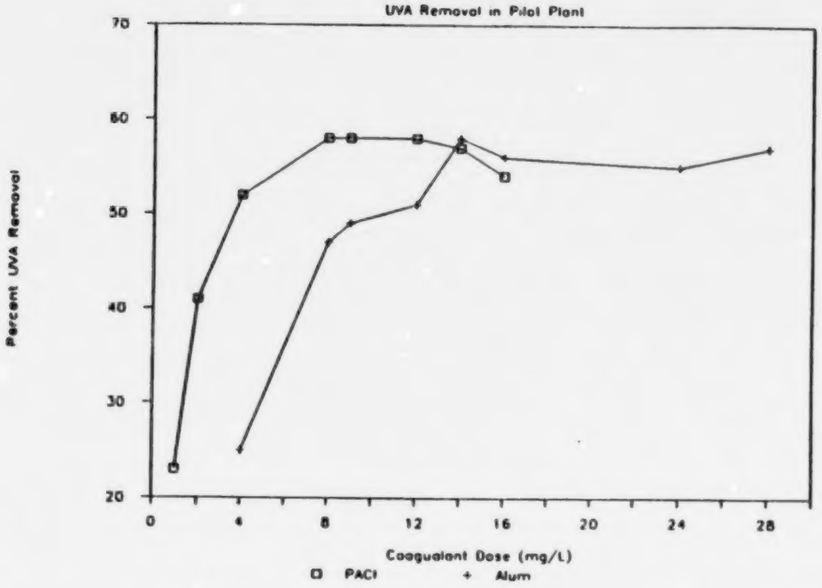
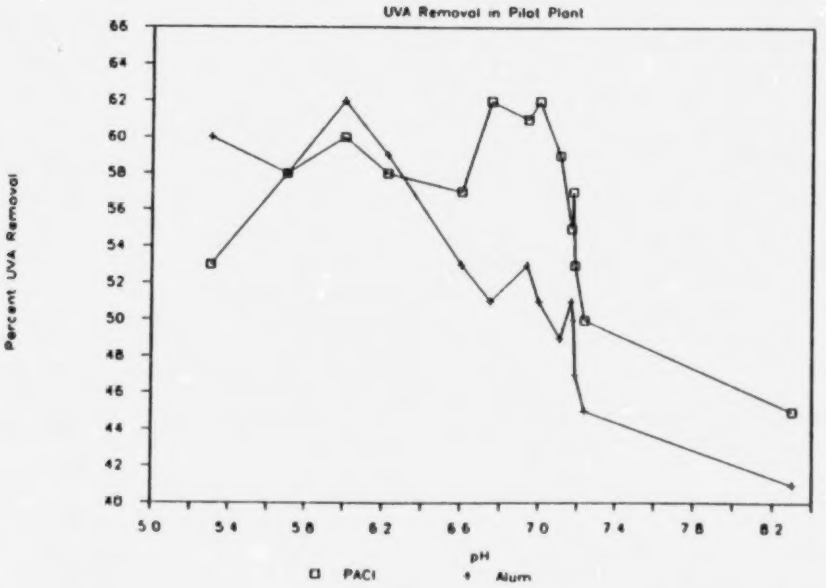

UVA Removal in Pilot Plant

FIGURE 8


UVA Removal in Pilot Plant

The results of this evaluation are shown in Figures 7 and 8, which respectively show the removal of UVA as a function of dose and pH, for both PACl and alum.

These results demonstrate that PACl and alum produce similar warm temperature water qualities in the pilot plant with respect to filtered water turbidity and UVA. The optimum operating conditions are approximately pH 7.2 at a dose of 8 mg/L for PACl, compared to pH 6.0 and a dose of 16 mg/L for alum. A more favourable operating pH condition for maximum UVA removal exists for PACl than for alum. These observations confirm the jar test evaluations, with the exception that the optimum dose of alum required in the pilot plant tests was 16 mg/L, an increase from the bench test determination of 12 mg/L. A cost comparison under these conditions, as conducted in evaluating jar test performances, resulted in a cost of \$8.75 / 1000 m^3 for PAC, compared to \$12.70 / 1000 m^3 for alum.

As a result of the cost comparison, it was decided to use PACl in the pilot plant tests, at a dose of 8 mg/L. Further pilot plant tests were conducted with PACl to better evaluate the best operating pH in the range of 6.9 to 7.2. Based on the results of this evaluation, an operating pH of 7.1 was selected.

Pilot Plant Evaluation of Conventional Treatment Process for the Removal of Spiking Chemicals

At the time of publication, only half of the results for the organics analysis were available. Thus, any evaluations made on the removal of specific SOCs are regarded as preliminary. A summary of the results of the first six analyses for the seven spiking SOCs monitored in this phase are contained in Table 1.

These initial results indicate that excellent removals were accomplished for decachlorobiphenyl (98.7%), 2,4,6-trichlorophenol (96%), and anthracene (82.2%). Intermediate removals of p,p'-DDT (51.6%), and pyrene (39.7%) were observed. There was virtually no removal of gamma-BHC and naphthalene.

A complete discussion of the results of this experiment cannot be made until the data set is complete. However, a general discussion regarding factors that possibly describe the relative amount of removal of the spiked SOCs can be made at this time.

If the relative magnitudes of some of the physical and chemical properties that influence removal are examined, then the removals of most of the spiked SOCs can be explained. For example, of the compounds considered here, naphthalene showed the lowest removal. In fact, no naphthalene was removed. Among the spiking compounds, naphthalene has the second highest solubility, the lowest octanol-water partition coefficient (Kow), the lowest Freundlich K (adsorption capacity), and has one of the lowest potentials for binding to humic materials. Thus, naphthalene is probably too soluble to be removed by precipitation. It is also likely to be too hydrophilic to be coprecipitated with other, more hydrophobic compounds present, and does not have enough affinity for particulates to be removed with them by colloid destabilization.

The same arguement can be extended to gamma-BHC to explain its presence in the finished water samples. Both pyrene and DDT are less soluble than either naphthalene or BHC, they have higher Kow

TABLE 1

SUMMARY OF INITIAL RESULTS OF CONVENTIONAL PROCESS EVALUATION

SPIKED COMPOUND	SPIKED INFLUENT	SETTLED WATER		FILTERED WATER	
		EFFLUENT	% REMOVAL	EFFLUENT	% REMOVAL
Decachlorobiphenyl	1.56	0.281	82.0	0.020	98.7
2,4,6-Trichloropenol	14.00	0.267	98.1	0.561	96.0
Anthracene	9.62	1.72	82.0	1.71	82.2
p,p'-DDT	2.63	1.68	36.1	1.27	51.6
Pyrene	7.44	5.57	25.1	4.48	39.7
gamma-BHC	4.72	3.84	18.5	4.70	0.4
Naphthalene	2.98	3.49	-17.3	3.26	-9.5

NOTE: All concentrations are in ug/L.

and Freundlich K values, and are more likely to bind to natural humics. It would therefore be expected that these compounds would be more readily removed than naphthalene or BHC, and the preliminary results support this. At the other end of the scale, decachlorobiphenyl shows the greatest removal. Amongst the SOCs studied here, it has one of the lowest solubilities, and some of the highest values for Kow and percent bound to humics. Therefore, there is a strong chance that decachlorobiphenyl will be removed with particulate matter by destabilization, or will be coprecipitated with, for example, metal fulvates.

The observed excellent removal of 2,4,6-trichlorophenol cannot be explained using these generalizations. This chemical has the highest relative solubility of the spiking group, and very low values for Kow, Freundlich K, and percent bound to humics. Using the arguments presented above, it would be expected that this compound would be very poorly removed. Other factors may be influencing the removal of 2,4,6-trichlorophenol, such as interactions of the functional group on the molecule with metal hydroxide products of the coagulant.

If the adsorption of the spiked SOCs onto the water contacting surfaces of the pilot plant is a significant factor in the removal of these compounds, then it must be stated that any removals reported in these experiments are an overestimation of the removal ability of the conventional processes. Adsorption of hydrophobic compounds will likely occur in a full scale plant as well, but the much larger surface area to volume ratio in the pilot plant makes this mechanism far more important on the experimental scale than on the full scale.

A more formal discussion of the removal of the spiking SOCs will be presented when the data set is complete.

The presence of acetone as a solvent in the stock solution of spiking chemicals rendered impossible any meaningful measurements of DOC and UVA in the treated water. However, immediately after the spiking compound sampling period was finished, the pilot plant continued to operate without spiking solution addition under the same coagulant dose, pH and raw water quality conditions. DOC and UVA measurements were then made. This gave a good indication of the removals of these parameters during the period of plant operation with spike addition. A summary of DOC, UVA and turbidity removals are shown in the table below, along with the performance of the Niagara Falls Water Treatment Plant in the removal of these parameters. A test for THMs was also conducted on samples from the pilot and full scale plants at Niagara. The pilot plant effluent samples were chlorinated in the lab to the same total chlorine residual present in the Niagara Falls WTP at the sample time. The result reported here is for the three day, utility THM test.

	RAW WATER					FILTERED WATER			
DATE	TEMP	TURB	COLOUR	DOC	UVA	TURB	DOC	UVA	THM
MAY									
Pilot Plant	8.1	2.2	<5	2.4	0.165	0.04	1.7	0.070	7.0
Niagara WTP						0.22	2.1	0.075	26.0
SEPTEMBER									
Pilot Plant	21.0	1.2	<5	2.1	0.159	0.05	1.3	0.066	
Niagara WTP						0.29	1.7	0.074	

This summary shows that the pilot plant performed consistently well in removing particulate and natural organic matter. Treatment in the pilot plant using PACl at a pH of 7.1 resulted in finished waters with lower turbidity and DOC levels than the Niagara Falls WTP. This plant employs alum as the sole coagulant, typically at a summertime dose of 10 mg/L, and operates at the ambient pH of 8.3. The significantly lower THM results for the pilot plant effluent may be partially explained by the prechlorination of settled water practised by the Niagara WTP. The pilot plant samples received only post chlorination. The operational summary indicates that filtered water turbidities below 0.1 NTU can consistently be achieved, and that DOC levels of around 1.5 mg/L can be reached under the proper operating conditions.

CONCLUSIONS

Alum, ferric chloride and polyaluminum chloride were all demonstrated to be able to successfully remove turbidity and natural organic matter from Niagara Falls raw water. Polyaluminum chloride produced an excellent quality of water at a higher pH, and was therefore to be the most economical coagulant to use.

The optimum pH and coagulant dose combination for use of polyaluminum chloride were found to be pH 7.0, and a concentration of 8 mg/L.

The use of secondary coagulants did not enhance the performance of the primary coagulants.

Polyaluminum chloride performed as well in cold water jar tests as in warm water. Alum was found to perform better in warm water.

When present in the raw water supply at concentrations around 10 ug/L, decachlorobiphenyl, 2,4,6-trichlorophenol and anthracene were found to be well removed by conventional treatment. This is based on preliminary observations. Pyrene and p,p'-DDT exhibited intermediate levels of removal, while gamma-BHC and naphthalene were shown to be very poorly removed.

QUANTITATIVE STRUCTURE-ACTIVITY RELATIONSHIPS FOR ORGANIC COMPOUNDS AND THEIR MIXTURES

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ABSTRACT

With MOE funding the ATRG has collected a comprehensive and detailed database on the acute and chronic toxicity and the bioconcentration of selected groups of organic chemicals: chlorinated benzenes, chlorinated phenols, and chlorinated ethanes and ethylenes, as well as some mixtures of these compounds. In addition, certain water chemistry and biological characteristics of the test organisms used, American flagfish and brook trout, were obtained. This information, in conjunction with literature data, will be used to address the following three objectives:

1). Refine and expand the currently established relationships between various molecular descriptors, toxicity test results, and bioconcentration.

2). Develop simple models to take advantage of the relationship between toxicant body burden and toxic responses to predict various toxicity test outcomes and their time course (i.e. kinetics), both for single chemicals and mixtures.

3). Incorporate provisions in the models for accounting for the influence of certain biological and environmental factors on the results.

As it is early in the project the presentation will focus on the current understanding of QSARs in Aquatic Toxicology, how the data set will be used, what outcomes are expected, and their ultimate utility.

Quantitative Structure-Activity Relationships For Organic Compounds and Their Mixtures

Introduction

One of the most difficult problems currently faced by regulatory agencies in general, and the Ontario Ministry of the Environment in particular, is the prediction and interpretation of toxic effects of environmental pollutants. The problem area is very broad, encompassing various media such as water, air, land, and food, various organisms, various effects, and various types of chemicals. We have chosen to focus on an area where we feel there is a good chance of success in establishing relationships which can be used both immediately in some practical applications, such as regulation development and enforcement, and in the future as a basis for more sophisticated investigations.

Specifically, we have chosen to study the acute and chronic toxicity, as well as the bioconcentration of selected organic chemicals (singly and in mixtures), in aquatic organisms. The objectives of the project are as follows:

1.) Refine and expand the relationship(s) between molecular descriptors, acute and chronic aquatic toxicity test results, and organism bioconcentration.

2.) Investigate biological factors, on both a intra- and interspecies basis, which may affect the accurate determination of the above relationships and examine methods of compensation and/or correction.

3.) Further investigate one-compartment, first-order, uptake, elimination, and metabolism constants generated from toxicity and bioconcentration data as well as factors influencing quantification. Also investigate the use of more sophisticated multicompartment models and non-first-order kinetics with this approach.

4.) Incorporate the above information and relationships into a simple microcomputer model which will provide a means interpolating and extrapolating bioconcentration and toxicity test data, both for some organic chemicals and mixtures and for several modes of toxic action.

Methodology

Data Set

For over the last seven years the Aquatic Toxicity Research Group of Lakehead University, with financial support from the Ontario Ministry of the Environment, has been carrying out aquatic toxicity research on a variety of organic chemicals. A summary of the chemicals and mixtures tested appears in Table 1.

Table 1. Organic Chemicals Tested by ATRG

1,4 - dichlorobenzene
1,2,4 - trichlorobenzene
1,2,4,5 - tetrachlorobenzene
chlorinated benzene mixtures

2,4,6 - trichlorophenol
2,3,4,6 - tetrachlorophenol
pentachlorophenol
chlorinated phenol mixtures

chlorinated benzene-chlorinated phenol mixtures

1,1,2 - trichloroethane
1,1,2,2 - tetrachloroethane
chlorinated ethane mixtures

trichloroethylene
tetrachloroethylene
chlorinated ethylene mixtures

chlorinated ethane-chlorinated ethylene mixtures

This research, which appears in ATRG project reports to MOE, represents a particularly unique and valuable data set for the objectives of this investigation. Not only were two test species employed, American flagfish, *Jordanella floridae* and brook trout, *Salvelinus fontinalis*, but acute toxicity, chronic toxicity, and bioconcentration data were collected by the same researchers under the same conditions and with the same fish stock. In addition, extra effort was expended to ensure that all analyses, including water characteristics, water and fish toxicant levels, and fish lipid levels, were particularly thorough. In many cases sampling was carried out more frequently than the minimum requirement and several analytical techniques were adapted or modified to improve accuracy.

This means that this data set is the most suitable of any available for the purposes of QSAR interpretation and modelling as many of the usual problems - different test organism stocks and species, varying water characteristics, different analytical protocols, etc. - have been minimized. Other data sets, such as the large acute toxicity data set of the U.S EPA-Duluth (Brooke et al., 1984; Geiger et al., 1984) and others, will be used for supplemental purposes but, despite the testing of many more chemicals, no other data set contains such a complete and thorough evaluation of the chemicals that were examined.

Investigative Procedures

The study can be divided into two basic parts: an investigative, evaluative portion and a modelling portion. The investigative portion will focus on refining and enhancing QSAR relationships currently established between various molecular descriptors, toxicity test results, and bioconcentration. The modelling portion will consider how best to incorporate the toxicokinetic information derived from the investigative portion of the study into functional models reflecting the physiology of aquatic organisms, the characteristics of the toxicants in question, and typical environmental conditions.

The concept of relating the biological activity of a chemical to its physical-chemical characteristics has been under study for over 100 years (Saxena and Ram, 1979). Quantitative structure-activity relationships are widely used in pharmacology where a variety of approaches are employed in addressing a diverse range of pharmacological/toxicological problems (Blankley, 1983). In the field of aquatic toxicity research the QSAR approach, for both toxicity and bioconcentration, has been receiving increased attention since the mid-1970's (Veith and Konasewich, 1975; Veith et al., 1979; Konemann, 1981; Mackay, 1982; Veith et al., 1983; Call et al., 1985; McCarty et al,, 1985). Although much of the work has focused on using the octanol-water partition coefficient (usually expressed as log P or log K_{ow}) researchers have been examining the use of other molecular descriptors, such as aqueous solubility (Abernethy et al., 1986), "solvatochromic" parameters (Kamlet et al., 1987), and molar volume (Abernethy et al., in press) and their relationships with octanol-water partition coefficients.

McCarty (1987 a) has, using log K_{ow} as the molecular descriptor, reported the following conclusions in study of acute and chronic toxicity, bioconcentration, and molecular descriptor interrelationships:

1. Acute and chronic QSARs, for the toxicants and species discussed, using log K_{ow} as the molecular descriptor, appear to be parallel, each having a slope of near unity.

2. The interrelationship of log K_{ow}, bioconcentration, and toxicity QSARs allows an internal (organism) toxicant concentration producing a defined biological response

to be established. Thus a means of quantifying and evaluating the toxicological significance of body burdens of organic chemicals, both singly and in certain mixtures is possible.

3. On the basis of this investigation it appears that the chemical potency or inherent toxicity of a variety of organic chemicals is relatively constant, when expressed in terms of the organism toxicant concentration. This is valid only for the nature of the biological responses studied (acute and chronic toxicity test results) and the type of toxic action examined (narcotic or narcotic-like toxicity).

For example, the body burden of toxicant associated with acute and chronic toxicity test endpoints for the narcotic chlorinated organic chemicals and aquatic organisms examined was estimated to be approximately 2.0 and 0.2 millimole/L (or per Kg if the density of the organism is approximately 1.0; McCarty, 1987a). The relationships for chlorinated phenols were similar, although less definitive, and indicated that body burden levels about ten times lower were associated with the test endpoints for this group of chemicals which are not considered to be narcotics (McCarty, 1986). Acute toxicity for a series of simple alcohols and ketones occurred at a body concentration of about 6.5 millimole/L (McCarty, 1987b). Other researchers have reported a similar phenomenon at a different biological endpoint; specifically, Mackay and Hughes (1984) in study of toxicant kinetics were able to determine that non-lethal narcosis (loss of equilibrium) in goldfish occurred at a body concentration of about 5 millimoles of toxicant per litre of fish.

Probably the most difficult problem faced by aquatic toxicologists, in their attempts to study and describe the events and processes of toxicity, is that in typical testing protocols the test organisms are treated as a "black box" and little or nothing is known of either the uptake and distribution or the mechanisms of toxicity. Although this has occurred primarily for technical, analytical, and cost factors, using the water toxicant concentration as a surrogate for the toxicant concentration in the organism is limiting, making interpretation of results a very complicated task. It has been a major stumbling block which has inhibited study of aquatic toxicity modelling. Associating a toxicant body burden with a definite biological response at an exposure time known to allow an approximate steady-state equilibrium between toxicant in the water and the test organisms provides a means to solve this problem.

McCarty (1987b) was able to show how the approximately constant body burden of toxicant associated with acutely toxic narcosis, derived from the interrelationship of K_{ow}, K_b, and toxicity as discussed above, could be exploited, in conjunction with first-order, one-compartment model assumptions, to estimate toxicant kinetic parameters. This was accomplished via non-linear curve fitting to time-toxicity data from typical LC_{50} toxicity tests. A preliminary study employing a small (14 chemicals) data set of simple alcohols and ketones concluded that:

1. The differences between the internal toxicant concentration endpoints for toxicity and bioconcentration are proportional to the bioconcentration factor.

2. This proportional relationship can be used to convert kinetics data from a bioconcentration basis to a toxicity basis and vice versa.

3. Quantitative Structure-Kinetics Relationships -QSKRs- can be constructed using one-compartment, first-order kinetics constants and a molecular descriptor.

The investigative portion of this study will be based on the concepts discussed above. The work will consist of employing the ATRG data set, as well as a broader sampling of the data in the published literature, to further study and refine interrelationship of molecular descriptor, toxicity, and bioconcentration and to use this to derive kinetic constants for use in the modelling portion of the study. Four major areas will be focused on:

1. The influence of choice of molecular descriptor on the interrelationship of molecular descriptor, toxicity and bioconcentration.

2. The effect of the mode of toxic action (where data on modes other than narcosis are available) on the character and nature of the QSARs.

3. The influence of environmental and biological factors, such as water characteristics, temperature, species, size, and lipid content, on the character of the QSARs.

4. The conditions and circumstances when the conversions between toxicity-based and bioconcentration-based kinetics data produces reliable data.

Modelling

Unlike the field of mammalian pharmacology, modelling in aquatic toxicology is a relatively recent development. Although modelling of bioconcentration has been carried out by aquatic toxicologists for some time (Spacie and Hamelink, 1982) the modelling of toxicity has been less successful as the actual amount of toxicant in the organism when a biological response occurs is usually unknown or not quantified (Zitko, 1979;

Mancini, 1983). Thus any toxicity-based kinetics data which is derived is usually of limited utility.

With the ability to quantify one-compartment, first-order kinetics constants from toxicity test data and to convert between toxicity- and bioconcentration-based kinetics constants the opportunity to begin realistically modelling toxicity is obtained. Although a wide variety of areas could be investigated the modelling portion of the study will focus on three areas:

1. Model type and level of sophistication.

The one-compartment, first-order kinetics model is the simplest approximation that can be employed. Although it will be adequate for the purposes of the initial investigations, more complex models should give better descriptions of the processes involved and results obtained. Four areas of concern are involved.

The first is the nature of the kinetics. Although first-order kinetics are often sufficient for describing many toxicant uptake and elimination results other types, such as zero order or Michaelis-Menten, may be appropriate is some cases. We will examine the data to determine if there are any benefits to be gained and if it is feasible to incorporate them into the model.

The second is the consideration of metabolism. It is usually assumed that, in the time frame of the typically employed toxicity and bioconcentration tests, metabolism of the toxicant is negligible. We will incorporate a provision for metabolism into our model and investigate if there is any benefit to attempting to account for metabolism with the data set being employed.

The third is the number of compartments. Multicompartment models are widely used in pharmacology and are capable of being more accurate than single compartment models. Although progressing to a two-compartment model may be possible, simply by viewing the organism as having separate lipid and aqueous phases, more physiologically accurate information on the size, chemical composition and blood perfusion of actual body compartments for aquatic organism of various sizes is required to realistically employ multicompartment models. We will be reviewing the literature to determine if sufficient data are available to attempt this.

The fourth point is the actual modelling technique that will be used. The discussion so far has been employing the conventional pharmacologic terminology and approach; however Mackay and his coworkers have been proposing the use of a somewhat different approach based on the concept of "fugacity". Fish toxicity and bioconcentration data has been successfully interpreted (Mackay and Hughes, 1984) and multicompartment mammalian models have been successfully described in terms of the fugacity approach (Paterson and Mackay, 1987). There is a distinct advantage in employing this approach as it has been validated for environmental scale toxicant fate modelling. We will examine the possibility of using this approach in tandem with the conventional approach.

2. Interpolation and extrapolation

In attempting to extrapolate the results to other circumstances the primary limitation will be the availability of addition data to test the hypotheses. There is some information on environmental conditions, such as temperature and pH, and they will be examined. Given the very significant impact of body size on kinetics - the surface area/volume ratio is a major influence on the rate of achieving steady-state equilibrium in objects or organisms of different sizes - and with fish spanning over many orders of magnitude in size, our primary goal in examining extrapolation will be attempting to provide a means of scaling the model to take into account differences in organism size.

interpolation will focus attempting to resolve the problem of the limited endpoints available from toxicity test data i.e. a concentration acutely lethal to 50% of the exposed population and a concentration based on the presence or absence of a non-lethal chronic effect. Mayer (unpublished) suggested that, for some aquatic toxicants, water toxicant concentration produced in a typical chronic toxicity test is essentially the same value as determined by estimating the probit value of the water concentration approximating 0% acute mortality in typical acute toxicity test data. This would explain the essentially parallel QSARs found for acute and chronic toxicity of narcotics by McCarty (1987a). We will further investigate this to determine if it is possible to associate body toxicant levels with intermediate, non-standard toxicity endpoints e.g LC 25 or LC 75, and thereby enable modelling to become a more diversified investigative and interpretive tool.

3. Mixtures of toxicants

Since, as noted earlier, within a particular mode of toxicity the organic chemicals of the group are essentially equipotent, the toxicity of mixtures of chemicals having the same mode of toxicity should be additive. However, estimating the toxicity of a mixture is not simple due to substantial differences in kinetics. Using the toxicity model we should be able to estimate the body concentration of each component of a mixture and then sum the total for comparison against body levels known to be associated with a biological response. Validation of the toxicity estimates for various exposure times and water toxicant concentrations will be attempted using the observed mixture toxicity data which was collected as a part of the ATRG research.

Expected Benefits of the Research

The utility of many of the benefits expected from this research will ultimately depend on the level of sophistication which can be achieved versus that which is appropriate for the problem in question. However, if this study achieves some reasonable level of success in addressing the goals which have been outlined above we expect to be able to generate a moderately simple computer model for interpolating and extrapolating typical aquatic toxicity test data, both for certain groups of organic chemicals and their mixtures . In the broadest sense such a model should provide a useful investigative research tool with both practical and theoretical aspects which ultimately should assist in improvement of the scientific basis for aquatic legislation development and regulation enforcement in the Province of Ontario.

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QUANTITATIVE STRUCTURE ACTIVITY RELATIONSHIPS FOR AQUATIC ORGANISMS

by

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Abstract

A series of relatively simple calculation procedures is described by which physical chemical data of a chemical can be used, in conjunction with estimations of water concentration (obtained from water quality models), to estimate bioavailability, bioconcentration, biomagnification, acute narcotic toxicity, and chronic toxicity for aquatic organisms. An example is presented to illustrate the procedure. A number of confounding factors are discussed.

Introduction

The purpose of this paper is to present a relatively simple and practical account of how Quantitative Structure Activity Relationships (QSARs) may be used to predict the bioaccumulation and certain toxic effects of organic chemicals in aquatic organisms. The procedure outlined is based on a research project which has been supported by the Ministry of the Environment, and has involved experimental measurements, theoretical interpretation of these results, and analysis of the results of other workers. The details of the experimental work and the theoretical background have been, or are being, published elsewhere. The project has lately involved collaboration with L.S. McCarty, formerly of the Ontario Ministry of Labour and now at the University of Waterloo, who has independently been pursuing a similar series of studies. We have benefitted greatly from several QSAR meetings, particularly two arranged by Dr. Klaus Kaiser, of the Canada Centre for Inland Waters, and one recently by the American Chemical Society and the Society for Environmental Toxicology and Chemistry in Denver, Colorado. The interested reader is referred to the references, which give most of the pertinent results and discussion, many of these papers being published in the above sources. In this paper, we focus on the practical application of the scientific findings.

We consider, as an example, a situation in which a lake is subject to relatively mild contamination by a number of organic chemicals, possibly of industrial and/or municipal origin. It could be a relatively well-mixed lake of volume 10^7 m^3 (say 1000 m by 1000 m by 10 m deep), with an outflow of water of 10,000 m^3/hour, giving a residence time of 1000 hours, or 42 days. Into this volume is emitted an effluent stream, possibly of municipal or industrial origin of 1000 m^3/h containing 1 g/m^3 or part per million of a specific chemical. If the chemical is conserved, ie. is non-reactive, then a simple steady state mass balance gives

$$\begin{aligned} \text{inflow} &= \text{outflow} \\ 1000\ m^3/h \times 1\ g/m^3 &= 10{,}000\ m^3/h \times C\ g/m^3 = 1000\ g/h \\ \text{therefore } C &= 0.1\ g/m^3 \text{ or } 100\ ug/L \end{aligned}$$

The standing or steady state concentration, C, will be 0.1 g/m^3 or 100 parts per billion. This is essentially an elementary water quality analysis or prediction. It is possible to include reaction of the chemical by, for example, biodegradation, exchange with the sediment, volatilization, and other processes in more complex water quality models. It is also possible to include stratification of the water column and treat time dependence. The essential point is that there is a body of knowledge and experience which can be used to take the loading data of 1000 g/hour and convert it into a standing concentration. It is noteworthy that this is the approach taken by the Ministry in the Water Quality track of the MISA program.

A recent IJC report (IJC, 1980) describes many such models in the context of the Great Lakes Basin.

The next and more difficult stage is to use such data for prevailing concentrations to draw conclusions about the impact of the toxic chemical. These analyses are essentially the subject of this paper. Our purpose is to demonstrate that, as a result of increased knowledge about the fundamental mechanisms of bioaccumulation and toxic effects, we can make some estimate the impact of these concentrations.

There are three effects which may be of environmental interest: bioaccumulation, acute toxicity, and chronic toxicity. We assume that the analyst has available information on the prevailing concentration from an actual measurement, or from a water quality model. Also available are details of the nature of the aquatic organisms present and those which may be notable by their absence. Information on the chemicals' properties is accessible.

We treat here only organic chemicals, not metals, organo-metals, or inorganic toxins such as cyanide or arsenic.

Chemical Properties

First, it is essential to have available information on chemical structure, molecular weight, and molar volume. These and other properties may be obtained from the literature, from handbooks, or from published estimation methods, for example, the CHEMEST system developed by Lyman et al. (1982).

Second, a most important property of the chemical is its lipid-water or octanol-water partition coefficient, K_{OW} (Hansch and Leo, 1979). This quantity can be obtained from the literature, measured, or there are available commercial data bases, such as CLOGP, which can be used to estimate it. It is usually reported as log K_{OW}, also known as log P. If water solubility information is available, it can also be used to estimate K_{OW} (Miller et al., 1985; Banerjee et al., 1980). The significance of K_{OW} is that it measures the hydrophobicity of the chemical or its tendency to partition into the lipid phases of organisms.

Third, it is useful to have some indication of the susceptibility of the chemical to metabolism, preferably in the form of a rate constant or a half-life. Unfortunately, such data are very difficult to obtain, but for most chemicals of environmental concern, metabolism rates are quite slow and a conservative, or worst case, assumption can be made that they do not react.

A recent very promising approach is to identify the structural features of the molecule which appear to convey degradability (Niemi et al., 1987). For example, in an analysis of biochemical oxygen demand (BOD) data, which is essentially a test of susceptibility to enzymatic conversion, these authors were able to identify a number of features, such as the presence of amino acid or aldehydic groups which impart degradability and t-butyl terminal groups or multiple substitution of a benzene rings which impart recalcitrance, ie. retard degradability.

Other information on the chemical which is of use includes any reported data on toxicity to a variety of organisms, vapour pressures, aqueous solubilities, sorption partition coefficients, bioconcentration, and biodegradability. Computerized processes, such as CHEMEST, can be used to estimate some of these properties if they are not available. It is noteworthy that there are considerable hazards in estimating these properties rather than measuring them directly, thus extreme caution should be exercised when estimations are used.

Bioaccumulation

First a few words of definition (Spacie and Hamelink, 1982). Bioconcentration generally refers to the process by which an organism (usually a fish), when exposed to water containing a concentration of chemical C_W, absorbs the chemical from the water and adopts a higher concentration C_{F1}. The ratio C_{F1}/C_W is a bioconcentration factor (BCF). The fish may also take up chemical from food to give an even higher concentration C_{F2}. The ratio C_{F2}/C_W is a bioaccumulation factor (BAF) and is usually measured in an actual lake, rather than in the laboratory. If the food concentration is C_E, then C_{F2}/C_E is sometimes referred to as a biomagnification factor (BMF).

Care must be exercised because authors use different definitions and biotic concentrations (and hence these factors) can be expressed on a wet, dry, or lipid (fat content) basis.

The simplest analysis is to assume that the organism of interest achieves equilibrium with water. A good first assumption is that the lipid portion of the organism is equivalent in properties and amount to octanol, then the concentration in organism lipids will be simply the product $K_{OW}.C_W$, where K_{OW} is the chemical's octanol-water partition coefficient and C_W is the water concentration. For example, if the water concentration is 0.1 g/m^3 and K_{OW} is 1000, then the concentration in the lipid will be 100 g/m^3. If the organism consists of 5% lipids, then the whole body concentration will be 0.05x1000 or 50 g/m^3. For most fish, lipid contents are in the range from 3 to 15%. Justification for this approach has been discussed by Mackay (1982).

There are at least eight possible reasons for deviation from this situation. .

1- If log K_{OW} is low, ie. less than 1, the substance (usually a very water soluble chemical, such as an alcohol) displays an almost equal tendency to partition between lipids and water. The result is that the extent of bioaccumulation will be underestimated, because a significant part of the chemical will be present in the water phases of the organism. A convenient "correction" is to add 1.0 to K_{OW} (not log K_{OW}) to account for this effect.

2- If log K_{OW} is very large, ie. greater than 6, bioaccumulation tends to be overestimated. This is a particular problem when log K_{OW} reaches 7 or 8. The reasons for this are not entirely clear, as has been discussed by Gobas, et al. (1987), but a simple procedure is to assume that chemicals with a log K_{OW} exceeding 6.5 have values of 6.5. This first order correction improves the prediction, but may still cause over estimation in some cases.

3- If the compound is subject to metabolism, then the bioaccumulation will be overestimated because the organism is able to degrade the compound internally. In such cases, the concentration in the organism will be less than calculated. It is very difficult with the present state of knowledge to predict the extent of this decrease. The best approach is to search for a reported, "field" bioconcentration factor. Examples of this are the polynuclear aromatic hydrocarbons which bioconcentrate less than expected because fish are able to metabolize them (Southworth et al., 1978).

4- There may be a food chain effect. That is, organisms receive chemical, not only from water, but by eating other organisms, and by doing so, they tend to increase their concentration above that in equilibrium with water. Again, the magnitude is difficult to assess, but a simple rule of thumb is that, for each step in the food chain, the concentration increases beyond that expected by equilibrium considerations by a factor of about 3. This applies for chemicals of log K_{OW} exceeding about 4. If log K_{OW} is less than 4, there appears to be an insignificant food chain effect. This effect is still not well documented, but will be in forthcoming publications (Oliver and Niimi, 1987; Connolly and Pederson, 1987).

5- It may be that the organism has not had sufficient time to take up the chemical and achieve equilibrium. This occurs particularly in laboratory situations. The effect tends to be that, when K_{OW} exceeds about 5, the organism has a lower concentration than expected. Growth also causes dilution of the concentration, and this may also contribute to concentrations which are lower than expected (Mackay and Hughes, 1984).

6- There may be reduced bioavailability of chemical in water, that is, not all chemical in water is truly in dissolved form and available for uptake. The primary competitor for, or sorber of, a chemical is any organic carbon-containing.matter suspended in water. If we assume that the organic carbon is equivalent to octanol, then the fraction of chemical which is in true solution is:

$$\text{Fraction dissolved} = 1/(1 + K_{OW}C_O)$$

where C_O is the organic carbon content of the water (g/g). Note that C_O is usually reported in mg/L, not g/g. For example, if log K_{OW} is 4 and C_O is 10 mg/L or 10^{-5} g/g, then the fraction dissolved is 0.91, 9% being sorbed and "unavailable".

7- The chemical may display unusual properties, for example, it may ionize, it may have surface active (or surfactant) properties, it may chelate, or it may vary in nature between metallic and organo-metallic forms. In such case, special treatment is necessary.

8- If the organism is benthic in nature, then the concentrations in it may be more indicative of those prevailing in the sediments than in the water column. Special treatment is again necessary. This issue has been discussed recently by Mackay et al. (1987).

It is emphasized that there is no substitute for carefully measured and reported field bioaccumulation factors. Second in preference is a reported laboratory bioconcentration factor, and third, the predicted factors outlined above.

For mixtures, the best assumption is that all chemicals behave independently, thus the total burden of chemical can be calculated from the sum of the individual burdens calculated as above.

Acute Narcotic or Non-selective Toxicity

The simplest manifestation of toxicity is narcosis, anaesthesia or non-selective toxicity. This has been widely studied and the results subjected to QSAR analysis. Narcosis is generally a rapid process and is usually reversible. It may not result in immediate death, but an organism which is subjected to prolonged exposure to narcotic concentrations inevitably dies. This is the usual test undertaken in the laboratory with a duration of 48 or 96 hours. Characterization of the nature of this process has been a major task of this Ministry sponsored research QSAR project, and from the results, we have developed a relatively simple procedure (Abernethy et al., 1987) which is based on the following principles.

The target site in the organism at which narcosis occurs is clearly organic in nature and has properties similar to, but not identical to, that of octanol. We can estimate a target-to-water partition coefficient from the chemicals' octanol-water partition coefficient, and then using the water concentration calculate what the concentration of the chemical at the target will be. We can then compare this concentration with the value which we believe causes the toxic effect. We prefer to calculate this target concentration in units of volume fraction because it is believed that the narcotic effect is caused by a "swelling" of some critical target tissues to the extent of only about 1% as a result of incorporation of a narcotic chemical. By volume fraction, we mean volume of chemical per unit volume of target tissue.

A note of caution is appropriate here. There is a considerable literature on narcosis and anaesthesia dating back nearly 150 years. In particular, there has been intense effort devoted to understanding the mode of action of anaesthetic gases in humans, but the topic remains controversial. The simple "swelling" model is consistent with the observations and can be used to generate a predictive correlation, but it may not represent the physiological reality (Evers et al., 1987).

An important feature of this simple analysis is that we treat all aquatic organisms as equivalent in sensitivity.

The first task is to calculate the target water partition coefficient, K_{TW}, from the octanol-water partition coefficient. We have developed the following equation:

$$K_{TW} = K_{OW}^{0.8} \quad \text{or} \quad \log K_{TW} = 0.8 \log K_{OW}$$

For example, if K_{OW} is 100,000, log K_{OW} is 5, K_{TW} is 10,000 and log K_{TW} is 4. We then calculate the product $K_{TW}.C_W.V.10^{-6}$ or y. The units of these quantities are important. K_{TW} is dimensionless. V, the chemical's molar volume, has units of cm^3/mol. For most chemicals, it lies in the range of 50 to 300 cm^3/mol and is the molecular weight (g/mol) divided by liquid density (g/cm^3). A simple procedure is to assume a density of 0.8, thus a molecular weight of 160 becomes a molar volume of 200. C_W is concentration in water in units of mol/m^3. If C_W is given in mg/L (or equivalently g/m^3), it must be divided by molecular weight to give mol/m^3. The factor 10^{-6} is used to convert from cubic centimetres to cubic metres. The product, y, is then the volume fraction of toxic chemical at the target site. As a result of our work and interpretation of that of others, we have established the following "rules":

If y exceeds 0.01, then a narcotic effect is virtually certain.

If y is less than 0.001, the narcotic effect is probably absent in the short term.

If y is intermediate, then the organism will be under stress, and its behaviour and performance will be adversely affected by the presence of the chemical, but it may not suffer short term incapacitation death. The cut off for exposure over a period of 2 to 4 days for 50% of organisms appears seems to be a value of y of about 0.006. We present later an example of such a calculation.

For mixtures, we again assume that all chemicals behave independently, calculate y for each chemical, then add them to give a total y. The total y can then be used to deduce the likely effect. This simple procedure can be used to check the acute toxicity of prevailing concentrations in lakes. It can also be used to estimate whether effluents, or regions close to effluents, are acutely toxic.

Again, there is no substitute for actual measurement of toxicity, thus if a measured LC50 is available, it should be used in preference to the estimation procedure.

Increasingly, we favour the use of smaller organisms which are able to respond more quickly to, but are not necessarily more sensitive to, chemicals. An ideal situation is one in which the effluent or water is subjected to a toxicity test, results are obtained, and these are interpreted using the above procedure. Strategies can then be adopted to remove the chemical(s) which contribute(s) most towards the toxic burden, ie. contribute most towards the total y. It is not always clear which this is, especially because chemicals vary enormously in their values of K_{OW} and K_{TW}, thus a low concentration of one chemical may have a much greater effect than a high concentration of another.

Again, there are several problems and confounding considerations. The most important is the time for uptake. Very large organisms may be slow to take up chemical of large K_{OW}, therefore, the narcotic effect may be considerably delayed. This is a particular problem in laboratory tests in which results are desired in a few days. The best procedure is to use smaller organisms which respond more rapidly, applying essentially the same principle as the mine canary. It is especially important for substances of high K_{OW} and low water solubility because these chemicals experience difficulty in moving through water phases to, and within, the organism. The problems of bioavailability and ionization are also important in this context.

Many chemicals prove to be considerably more toxic than is estimated by this route. These tend to be electrophiles and exert a specific toxic effect. They are involved in specific chemical interactions with chemical constituents of the organism. It is also possible that the chemical forms metabolites or other breakdown products which are more toxic than the parent chemical. An example which we have come across experimentally, and in the literature, is anthracene, which photolyzes and gives rise to active oxygen species which exert the primary toxic effect (Oris and Giesy, 1985).

Chronic Toxicity

For chronic toxicity, we use a similar approach to that discussed by McCarty (1985, 1987). Again, we calculate an individual or, in the case of a mixture, a total y. The limits of y are much less well defined, because the experiments are much more difficult to conduct and data are sparce. From an analysis of the literature, McCarty has concluded that concentrations about a factor of 10 less than the acute values cause chronic effects. Others use a more conservative factor of about 25 (Ralston, 1987), and in Michigan, a factor of 45 is used to ensure that the procedure is correct in 80% of the cases. The ratio of acute to chronic toxicities, or LC50s, varies considerably between chemicals and between organisms. For example, in the Michigan DNR analysis (State of Michigan, 1984), this ratio varies from 1.35 for hexachlorocyclopentadiene to 472 for beryllium. Many metals have very large ratios which can be interpreted as a situation in which a toxicant acts in a slow, subtle manner; a low concentration causes death in the long term, but a large short term dose can be tolerated. The use of a factor of 10 to 15 gives a fairly reliable result, but greater assurance that the results are conservative can be obtained by increasing it to 25 (70% "correct") or 45 (80% "correct"). We use the same rules as before, but divide each y by a factor of 10, ie.
- if $y > 0.001$, chronic toxicity is certain
- if y is 0.001 to 0.0001, chronic toxicity is probable
- if y is 0.0001 to 0.00001, chronic toxicity is unlikely but possible
- if $y < 0.00001$, chronic toxicity is almost certainly absent

It is notable that other subtle effects may occur, for example, failure to feed, failure to resist or avoid predators, failure to reproduce or interference with chemo-sensing systems. These effects can destroy a population, although the individual organism continues to function. This analysis again applies only to non-selective toxicity.

Genotoxic Effects

At present, these effects are not treated by this analysis, and a chemical by chemical assessment is needed. Attempts are being made to develop structure-activity relationships or analysis based on the presence of certain structural groups, such as nitrosamines, but this issue is beyond our scope here.

Discussion

The aim of this paper has been to present a relatively simple procedure for calculating bioaccumulation and non-selective toxicity. It contains some elements of speculation and much more data are needed for a variety of chemicals and organisms before it can be fully validated. We believe that the focus of current research should be on smaller organisms because they respond more rapidly. The tests are faster, less demanding of time and resources, and are cheaper. There is a real need to develop better predictive capabilities for a variety of organisms and to obtain more chronic data. There is also a need to develop and standardise more tests covering a variety of organisms. Table 1 gives an example of current thinking about a suite of tests suitable for Canadian conditions (Environment Canada, 1987). Using the procedure outlined here, it is possible to make a judgement about likely toxic effects. The tendency will be to underestimate the toxicity, especially for chemicals which have high activity. Lipnick (1987) has recently discussed the nature of these chemicals, and the reader is referred to that paper for more details.

Finally, we emphasize that there is no substitute for actual measured values of toxicities or bioaccumulation parameters. Unfortunately, for many of the chemicals of concern in Ontario waters, such data are not available, and we are forced to resort to estimation procedures. Such estimation procedures also serve to "check" the reasonableness of reported laboratory or field data. It is hoped that, as a result of further investigation and theoretical analysis, it will be possible to refine the process sketched here to provide a more reliable organism-specific method of calculating the impact of organic chemicals on aquatic ecosystems.

Table 1. National Core Aquatic Toxicity Tests for C&P Laboratories

Test Type/Response	Test Species
Lethality[1]	
freshwater fish - mortality	Salmo gairdneri (rainbow trout, kamloops, steelhead)
estuarine/marine fish - mortality	Gasterosteus aculeatus (3-spine stickleback)
freshwater invertebrate - mortality	Daphnia magna (water flea)
marine invertebrate - mortality	Artemia sp. (brine shrimp)
marine invertebrate - mortality	[Rhepoxinius abronius (amphipod)]
Sublethality	
freshwater fish - ATP stress (physiological)	Salmo gairdneri
freshwater fish - larval growth inhibition	Pimephales promelas (fathead minnow)
freshwater invertebrate - reproduction	Daphnia magna/Ceriodaphnia reticulata[2]
freshwater algae - growth inhibition/stimulation	Selenastrum capricornutum or others
bacteria - luminescence inhibition (metabolic)	Photobacterium phosphoreum
Genotoxicity	
bacteria - Dark Mutant Test/SOS Chromotest/Ames Test[3]	Escherichia coli/E. coli/Salmonella typhimurium
Bioavailability	
freshwater and marine fish - bioaccumulation	S. gairdneri, G. aculeatus, P. promelas
marine mollusc - bioconcentration	[Macoma balthica (clam)]
Biodegradability	
mixed aerobic bacterial culture (OECD series)	

1. includes incapacitation/immobilization
2. species to be addressed in protocols
3. alternative tests for indicating genotoxicity

[ ] denotes tests and/or species being evaluated for potential use in Ocean Dumping Control

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Appendix

Example of QSAR Application

Table A 1 gives data for four hypothetical chemicals and their concentration in the lake discussed earlier.

The lake has a volume of 10^7 m^3 and receives a total flow of 10^4 m^3/h, giving a residence time of 1000 hours. There is an effluent of 1000 m^3/h containing these four chemicals at various concentrations. The lake is observed to have an unstable fish population with periodic fish kills. It is suspected that there is no fish reproduction.

We discuss each chemical in turn, calculating the prevailing concentration from the measured loading, then interpreting the bioconcentration and toxicity calculations using QSAR techniques.

Table A 1

Chemical	A	B	C	D
Molecular mass (g/mol)	160	180	200	300
Molar volume cm^3/mol	200	230	250	375
log K_{OW}	3	4	5	6.5
Effluent conc. g/m^3 or mg/L	10	3	.01	60×10^{-6}
Loading g/h	10000	3000	10	0.06
Lake conc. g/m^3	1	0.3	.001	6×10^{-6}
Lake conc/ mol/m^3	0.006	0.0017	5×10^{-6}	20×10^{-9}
Bioconcentration factor (1)	50	500	5000 [500](5)	158000
Fish conc. ug/g	50	150	5[0.5](5)	1.0(6)
log K_{TW} (2)	2.4	3.2	4	5.2
K_{TW}	252	1580	10000	158000
y (3)	0.0003	0.0006	0.00001	10^{-6}
Expected acute LC50 g/m^3 (4)	19	3	0.5 [0.02](5)	0.03

Notes.

(1) K_B calculated as 0.05 K_{OW}

(2) log K_{TW} is 0.8 log K_{OW}

(3) y is Lake conc. (mol/m^3) x K_{TW} x Molar vol. x 10^{-6}

(4) Acute LC50 estimated as 0.006/(K_{TY}.Molar vol.10^{-6})

(5) Reported values, in parentheses, differ from QSAR values suggesting that the QSAR analysis is in error

(6) Food chain magnification to 3 and 9 ug/g is expected

Chemical A is similar to a dichlorobenzene, is conservative, and is discharged into the receiving water at a high rate of 10 kg/h, resulting in a standing concentration of 1 g/m^3 or ppm. Although the bioconcentration factor is low (50), the fish concentration is expected to be fairly high (50 ug/g or ppm) because of the high water concentration. The estimated volume fraction in the target narcosis tissue (y) is 0.0003 or 0.03%. This is probably not acutely toxic, but is possibly chronically toxic. The acute LC50 is expected to be about 0.12 mol/m^3 or 19 g/m^3, a factor of 19 higher than the prevailing concentration in the lake.

Chemical B is more hydrophobic and is similar to a tetrachlorobenzene. The load is 30% that of A, resulting in a correspondingly lower concentration (0.3 g/m^3). The bioconcentration factor is 10 times higher, thus fish concentrations are expected to be very high and about 150 ug/g, rendering fish inedible. The y value is 0.0006, which is almost certainly chronically toxic, thus the water will be unable to sustain a permanent population. Further, the total y for chemicals A and B is 0.0009, which is close to the level at which acute effects are expected.

To reach a y below 0.0001, at which there is hope of maintaining a stable population, would require reducing discharges of A by a factor of 10, and preferably about 20 for B. Because of its greater hydrophobicity, lower concentrations of B must be established.

Chemical C is still more hydrophobic and is similar to a polynuclear aromatic hydrocarbon. The load is only 10 g/h, giving a low concentration of 0.001 g/m^3 or 1 ppb. K_B is "expected" to be about 5000, but literature reports are of values of 500. It appears that this chemical is metabolized, thus prevailing fish concentrations are about 0.5 ug/g instead of 5 ug/g. The y value is 0.00001, which is very low. The expected acute LC50 is about 0.5 g/m^3, but there is a reported value of 0.02 g/m^3, a factor of 25 lower and thus more toxic. It appears that this may be a selective toxicant, causing other-than-narcotic effects. Despite the low y value, some chronic effects may occur. The chemical thus has unusual properties and needs custom treatment.

It appears that some discharge reduction is warrented, but it is difficult to quantify the desired magnitude.

Chemical D is very hydrophobic and is similar to a PCB. Fortunately, the discharge is only 0.06 g/h, and the effluent concentration is a barely detectable 60 ug/m^3 or 0.06 ug/L or ppb. The lake concentrations are a factor of 10 lower or 6 ng/L. But the bioconcentration factor is 158000, giving a fish concentration of 0.95 ug/g or ppm. The y value is negligible (10^{-6}), thus there will be no chronic or acute effects. The difficulty is that D is believed to be a human carcinogen, and levels exceeding 0.5 ppm in food are undesirable. The issue is further complicated by an expected food chain biomagnification effect which could result in higher trophic level fish having concentrations 3 or 9 times larger, which definitely exceed human consumption guidelines.

A discharge reduction of a factor of at least 20 to 0.003 g/h is indicated to protect human health. There is no problem of toxicity to fish. In the longer term, "virtual elimination" is desirable.

In summary, the QSAR analysis enables the loadings of A, B, C, and D to be translated into statements of bioconcentration and toxicity, individually and collectively. Each contaminant has its own "character" and set of special considerations. The strategy in water quality analysis must be to develop fate models, including terms for transport and tranformation to enable reliable estimates of concentration to be made. These can then be compared with measured values in water and sediments. A toxicity assessment can then be done, preferably using reported BCFs and LC50, but using QSAR values to fill gaps, check reasonableness and help interpretation. Finally, the magnitude of the desired individual discharge reductions can be assessed and compared with what is achievable using best available technologies.

It is hoped that this example will
(i) encourage others to undertake and report similar but real analysis
and (ii) serve to justify further research into QSARs by illustrating how
the science may be used in a regulatory context.

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TOXICITY OF A TECHNICAL FORMULATION AND PURE PENTACHLOROPHENOL TO THREE SPECIES OF ZOOPLANKTON (ACUTE/CHRONIC) AND FIELD STUDIES

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INTRODUCTION

Pentachlorophenol (PCP) has been used extensively in North America primarily as a wood preservative in forestry, and a biocide in agriculture. It is believed to be the most toxic of the chlorophenols (CP) which have recently come under review by the pesticide regulatory authorities and pentachlorophenol has been put on the list of priority chemicals in Category II.

One of the major concerns with the use of this chemical is that the technical formulations may be contaminated with potentially more dangerous compounds (i.e. phenoxyphenols) which may serve as precursors for dioxins. There is also some suggestion that the transformation products of PCP may in fact be more toxic than the parent compound. With this in mind a laboratory study was initiated to compare the acute and chronic toxicity of pure pentachlorophenol and a technical formulation of PCP to three species of daphnia.

Standardized, static, 48 h toxicity tests (Kaushik and Stephenson, 1986) were used to determine the acute toxicity of pure pentachlorophenol and technical PCP to three age classes of *Daphnia magna* and adult *Daphnia galeata mendotae*. The toxicities of both forms of PCP on *Daphnia pulex* have also been assessed. From these laboratory derived data, we were able to make a number of predictions regarding the impact of PCP on the zooplankton communities of a lentic ecosystem. The 'limnocorral technique' developed at the University of Guelph (see Kaushik et al. 1986, for review) provided us the means with which these predictions could be evaluated under conditions that better simulated a natural lentic environment. The major objective of this study was to assess the impact of an application of 1.0 mg/L pure pentachlorophenol on the plankton communities in large volume in situ enclosures or limnocorrals. The concentration of PCP applied approximated the midrange value of the LC50 estimates for the three species of daphnids.

MATERIALS AND METHODS

Six limnocorrals (5x5x5 m deep) located in Lake St. George (10.3-ha, 43^{o} 57'25''N, 79^{o} 26'30''W) were lined with ultraviolet protected polyethlene (6 mil) and the sides were lowered on May 17, 1987. Details on the design, construction and installation of the limnocorrals have been described by Solomon et al. (1980) and Kaushik et al. (1986). The walls isolated a column of water from the surface of the lake to and including the bottom sediments.

On June 17, 1987 pure pentachlorophenol (99.9%, Aldrich Chemical, Milwaukee) was dissolved in 1 L of 1 M NaOH and mixed with approximately 5 L of lake water in a back-pack sprayer. The solution was then applied uniformly to the surface waters contained within an enclosure to give a nominal concentration of 1.0 mg/L PCP. Pentachlorophenol was applied to three limnocorrals and the other three control corrals remained untreated.

Collection of biological samples

The enclosures were sampled weekly during the pretreatment period and on days 1, 4, 8, 15, 22, 29, and 43 posttreatment. Five 1 L water samples were collected with an integrated tube sampler and pooled (Solomon et al. 1982). A 1 L subsample was processec in the laboratory within 12 h and sent to the Canadian Centre for Inland Waters, Burlington, Ontario for nutrient analyses (dissolved organic carbon, dissolved inorganic carbon, total nitrogen, total filtered phosphorus, total unfiltered phosphorus, the major ions, total nutrients, hardness, alkalinity, particulate organic carbon and nitrogen, and chlorophyll). Plankton samples were collected with an integrating tube sampler (Solomon et al. 1982) and preserved in the field. The zooplankton samples were identified and counted in the laboratory as described by Stephenson et al. (1984), however, with some modifications. The macrozooplankton were counted using a compound micropscope and rectangular counting chamber with a grid. Aliquots that ranged from 1 to 4 mL, depending on the density of organisms, were transdferred to the counting chamber and the total subsample counted. If necessary additional aliquots were counted up to three subsamples or 300 organisms, whichever came first.

Physical and Chemical Measurements

Temperature and oxygen were recorded in each corral with a YSI dissolved oxygen-temperature meter (model 57) at the surface and depths of 0.5, 1.5, 2.5, and 3.5 m. The relative transparency of the enclosed water was ascertained by secchi readings and the pH measured.

Collection of samples for PCP Residues

A 1 L water subsample from the pooled water samples collected with the integrating tube sampler (5 L) was preserved immediately in an amber bottle with approximately 1 mL concentrated HCl and these samples were analyzed for PCP residues. Sediment samples were collected for residue analyses using the sediment sampler described by Solomon et al. (1987). Polyethylene strips made from the liner material were suspended in the corrals at the onset of the experiment and these strips were collected at regular intervals for analysis for PCP residues that may have adsorbed to the material.

PCP Residue Analyses

An aliquot (1 or 10 mL) of the acidified field sample, depending on the sampling date, was added to 100 mL 0.1 M potassium carbonate solution. 20 mL of hexane was added, followed by 1.5 mL double distilled acetic anhydride. This solution was then placed on an orbital shaker (200 rpm) for 1 h. The hexane layer was then collected after filtering through sodium sulfate, to ensure removal of all water, and approximately 4 mL of isooctane was added. The sample volume was reduced to approximately 1-2 mL using an analytical evaporator (nitrogen gas) and the remaining isooctane-chemical complex transferred to a volumetric flask and isooctane added to accurately measure 10 mL. An aliquot of this sample was then analyzed on a Perkin-Elmer sigma b gas chromatograph, equipped with an AS-100b autosampler and an electron capture detector. The carrier gas was hydrogen and the flow gas argon/methane. The capillary column used was a DP-5 (30 m long, fused silica, 0.25 μ film thickness).

RESULTS

Preliminary analyses of water on day 1 indicated that the PCP application to the three treated enclosures resulted in PCP levels close to the desired nominal concentration of 1.0 mg PCP/L (Table 1). The initial concentrations varied slightly due to minor differences in the volume of water within each of the enclosures. The dissipation of PCP in the water column of the treated corrals indicated that by day 8 posttreatment, the mean concentration of PCP in the treated enclosures was less than 10% of the initial application. Analysis of samples for PCP residues is still in progress but the dissipation of PCP from the water column appears to follow first order kinetics.

Table 1. Concentration of pentachlorophenol in enclosures treated with a nominal concentration of 1.0 mg PCP/L.

Number of days after application of PCP	Corral Number 1	2	3	Mean (SD) mg/L
1	0.840	0.985	0.905	0.910 (0.073)
4	0.460	0.690	0.570	0.573 (0.115)
8	0.120	0.060	0.073	0.084 (0.032)

Table 2. Mean temperature ± SD (°C) at two depths in control and PCP treated corrals.

No. of days before/after PCP application	Depth (m) 0.5		3.5	
	Control	PCP	Control	PCP
-6	20.0 (0.5)	20.0 (0.5)	15.2 (0.3)	14.8 (0.3)
-1	22.8 (0.3)	22.8 (0.3)	15.8 (0.3)	16.0 (0)
4	24.2 (0.3)	23.0 (0)	16.1 (0.1)	15.7 (0.3)
8	26.0 (0.5)	25.0 (0.5)	17.2 (0.3)	17.7 (0.3)
15	22.2 (0.3)	22.2 (0.3)	18.0 (0)	17.8 (0.3)
22	25.2 (0.3)	24.5 (0)	19.2 (0.3)	19.0 (0)
29	24.3 (0.6)	23.8 (0.3)	19.5 (0)	19.0 (0)
43	26.0 (0)	25.3 (0.3)	19.1 (0.1)	19.2 (0.3)

Table 3. Mean pH values for water collected from control corrals and corrals treated with 1.0 mg PCP/L. (- is before, + is after treatment).

Days (+/-) treatment	Controls	PCP
-6	8.27 (0.12)	8.17 (0.15)
-1	8.07 (0.12)	7.93 (0.12)
4	8.33 (0.16)	8.27 (0.06)
8	8.37 (0.06)	8.30 (0.10)
15	8.03 (0.06)	8.10 (0.10)
29	7.87 (0.15)	7.83 (0.15)
43	8.20 (0.10)	8.03 (0.06)

Table 4. LC50 estimates for *D. magna* exposed to pentachlorophenol.

Life stage	Exposure duration	Toxicity (mg/L)	Experimental conditions	Reference
Young	48	1.05		Adema & Vink (1981)
Adult	48	1.40		"
Young	48	1.0	fed, 20oC	Adema (1978)
Young	48	0.6	not fed, 20°C	"
Adult	48	1.5	fed, 20°C	"
Adult	48	0.8	not fed, 20°C	"
-	48	0.68	pH 8.0, 22°C	LeBlanc (1980)
-	48	0.260	pH 8.0, 20°C	Canton & Adema (1978)
-	48	0.400	pH 8.0, 20°C	"
Young	48	0.44	hardwater	Berglind & Dave (1984)
	48	0.5	softwater	"

There was no change in pH of the water exposed to pentachlorophenol (Table 3) and the temperature profiles at the various depths were similar in all corrals (Table 2). The data regarding the chemical composition of the water (i.e. nutrients) are not yet available.

Secchi depth readings varied greatly among replicate corrals for both the controls and the PCP corrals; however, greatest divergence between treatments occurred immediately after the pesticide was applied (Figure 1). There was greater transparency of water in the PCP corrals.

Mean concentration of oxygen in the water at a depth of 0.5 m showed a decline in the PCP treated corrals immediately posttreatment (Figure 2), but again the variability among the replicate enclosures was extremely high, especially for the control corrals. At the lower depth of 3.5 m (Figure 3), there seemed to be little difference in oxygen concentration and the tremendous variabilty was attributed to the presence of a hypolimnion in two of the enclosures.

The plankton were divided into two groups, the microzooplankton or Rotifers and the macrozooplankton or crustacean zooplankton which included the Cladocera, the adult Copepoda (Cyclopoids and Calanoids) and the immature Copepoda (nauplii and copepodites). PCP at 1.0 mg/L was not directly toxic to the macrozooplankton and the mean numerical densities in the treated enclosures did not differ from those in the control corrals (Figure 4). However, there appeared to be a numerical decline in densities of Rotifers immediately posttreatment with recovery to levels similar to those in the control corrals within 15 d (Figure 5). Statistical analyses of these data is in progress.

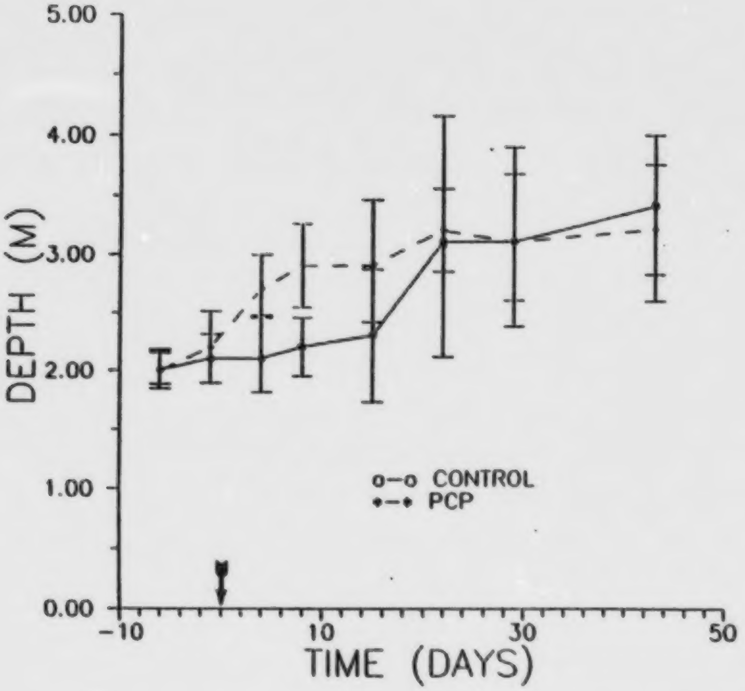

Fig. 1. Mean (± SE) secchi readings in control and PCP treated enclosures (↓ PCP application).

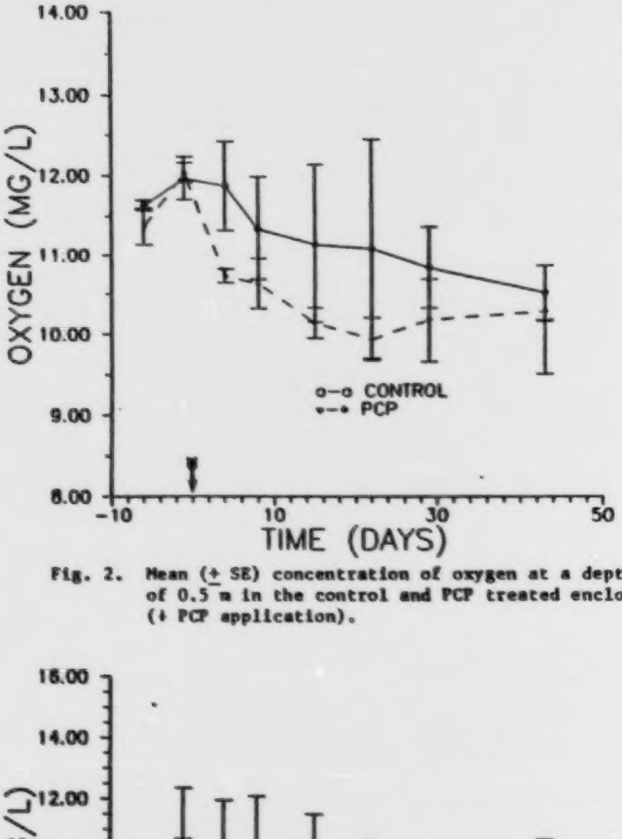

Fig. 2. Mean (± SE) concentration of oxygen at a depth of 0.5 m in the control and PCP treated enclosures (↓ PCP application).

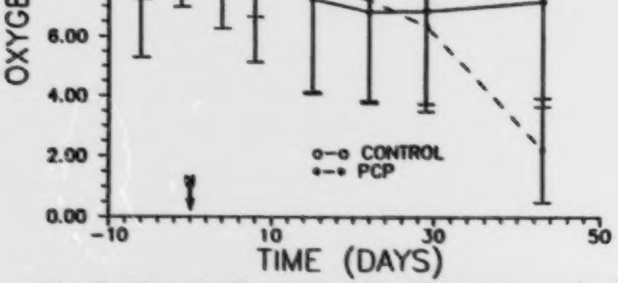

Fig. 3. Mean (± SE) concentration of oxygen at a depth of 3.5 m in control and PCP treated enclosures (↓ PCP application).

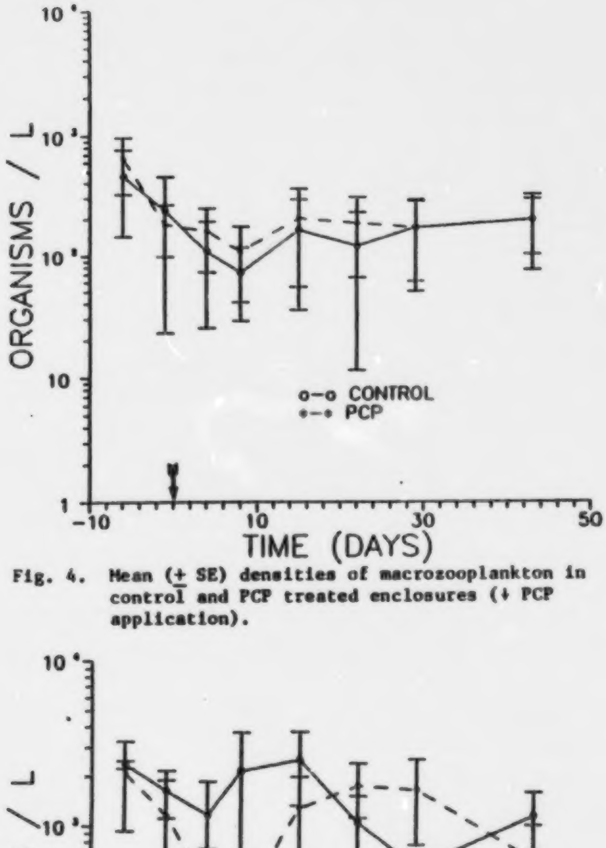

Fig. 4. Mean (± SE) densities of macrozooplankton in control and PCP treated enclosures (↓ PCP application).

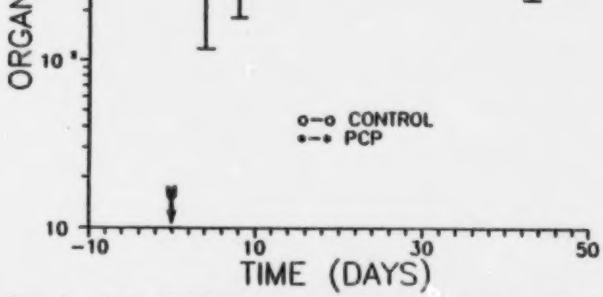

Fig. 5. Mean (± SE) rotifer densities in control and PCP treated enclosures (↓ PCP application).

DISCUSSION

To date not all of the information from the study is available so some of our predictions have yet to be tested. However, results do indicate that the PCP dissappeared from the water more rapidly than expected and this was attributed to photolysis. We applied the chemical via direct surface spraying between 1100 and 1300 h on a day that was clear and sunny with a mean temperature of 25°C. Within a couple of hour after the PCP was applied, the water within the treated corrals became brown in colour, most likely the result of photochemical degradation (Dr. J. Carey, pers. comm.). The photolysis apparently occurred when the pesticide was most concentrated at the surface. No water samples were collected from discrete depths for analyses for pesticide residues so the rate with which the PCP penetrated the water column was unknown. Methoxychlor applied in this manner penetrated the water column within 24 h (Solomon et al. 1986) and there was no reason to believe PCP would behave differently. Because of the impact of photolysis on the diurnal application of PCP, the toxicity of PCP to the biota was believed to be minimized.

In laboratory studies pentachlorophenol was toxic to adult *D. magna*, *D. g. mendotae* and *D. pulex* at 1.8, 0.058, and 5.8 mg PCP/L, (48h-LC50) respectively. The mean LC50 estimate for adult *D. magna* was higher than many that were found in the literature (Table 4). Initially, it was suspected that age of test organism (i.e. adult versus young) would explain this difference; however, futher investigation showed that pure PCP was equally toxic to young (24 h) and juvenile (24-48 h) *D. magna* with 48h-LC50 estimates of 1.50 and 1.54 mg PCP/L, respectively. Adema (1978) also found that age of test organisms did not affect toxicity of PCP to this species. There were no obvious differences in temperature or pH of the test solutions that may have explained the difference in toxicity values, and apparently hardness does not affect toxicity of PCP to daphnids (Berglind and Dave, 1984). However, comparable LC50 estimates were documented by Adema (1978) in a study comparing the toxicity of PCP to young and adult *D. magna* that were starved or fed. When the animals were fed algae, the LC50 estimates were 1.0 and 1.5 mg PCP/L for young and adults, respectively. The organisms in our assays were fed green algae, an libitum, prior to each test, thus we speculate that the relative difference in toxicity estimates may be attributed to "conditioning" of the test organisms.

The 48h-LC50 estimates for *D. g. mendotae* and *D. pulex*, both of which were present in Lake St. George, established a response range on which to base predictions regarding toxicity of an application of 1.0 mg PCP/L to the enclosures. We predicted differential toxicity to the Cladocera with some species exhibiting less resilience than others. On the basis of past experiments with pesticides applied to limnocorrals in this lake ecosystem (Kaushik et al. 1985; Stephenson et al. 1986), we predicted that there would be direct toxicity to the macrozooplankton, with evidence of some species being less resilient than others, and little impact on rotifer densities. Therefore, the decline in densities of Rotifera immediately posttreatment was as unexpected as was the apparent lack of toxicity to the cladoceran crustaceans. Studies regarding the impact of pesticides to rotifers are rare, despite being a major component in lentic ecosystems. Further laboratory research is necessary to more fully describe the toxicity of PCP to this group of aquatic organisms. The lack of toxicity to the macrozooplankton may be explained, in part, by the mode and time of day of the application of PCP to the enclosures.

A large amount of variability among replicate enclosures within treatments prevailed throughout the experiment and this variability, indicated by the error bars on the population point estimates in Figures 4 and 5, obscured what may have been a statistically significant impact of PCP on the rotifer communities. The varlabilty within replicate corrals resulted from differences in community structure. For example, on day -1 two of the control corrals had extremely high rotifer densities and correspondingly low macrozooplankton densities. But the third control corral had high macrozooplankton densities and low rotifer densities. The PCP enclosures were similarily populated. This variation in community structure was believed to have influenced secchi depth readings and oxygen concentration, contributing to the variabilty in these parameters. Chlorophyll data would also be expected to mirror the differences among corral replicates.

It was believed that one of the major factors contributing to this variation in zooplankton community structure in replicate corrals of both the control corrals and the treated enclosures was the presence of fish during the pretreatment period. In the past the enclosure walls have been lowered before the eggs of planktivorous fish hatched and the problem has not been magnified to this extent. A second experiment was conducted to compare the impact of an application of PCP at night when photolysis was hopefully minimized and fish were removed from all of the corrals by nets. Results from this second experiment are not yet available.

Acknowledgements

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Ultraviolet Disinfection: Its Effect on *Escherichia coli* and Bacteriophages as Indicators of Disinfection Efficiency of Wastewater

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The disinfection of wastewater with ultraviolet (UV) light has been accepted throughout North America as an alternative to the use of chlorination (United States Environmental Protection Agency, 1986).

This study looked at two aspects of UV disinfection to determine its ability to eliminate pathogenic microorganisms from wastewater. UV irradiated *E. coli* was studied *in situ* to determine the significance of photoreactivation in the natural environment and two methods were used to study the suitability of bacteriophages as indicators of the viricidal efficiency of UV disinfection. Part A of this report will describe the former study and Part B the latter work.

PART A: *In situ* Photoreactivation of *E. coli*

The inactivation of microorganisms by UV radiation results primarily from the absorption of the light by their DNA and the resultant dimerization of thymine bases in the DNA. These thymine dimers distort the conformation of the double helix and interfere with normal DNA replication. This photo-dimerization can also occur with the uracil in the RNA of viruses (Harm, 1980). The germicidal effect of UV radiation is greatest in the far-ultraviolet wavelength (190-300nm) range (Jagger, 1967). Subsequent exposure of UV damaged cells to higher wavelength light (above 300 nm) may often repair much of the damage to the DNA. This light-activated enzymatic pyrimidine monomerization process is termed photoreactivation (Jagger, 1967). Many different microorganism can undergo photoreactivation (Harm, 1980). Enteric pathogenic bacteria have been shown to photoreactivate (Jagger, 1958).

Photoreactivation of fecal and total coliforms can occur after UV disinfection of wastewater. Scheible and Bassell (1981) placed bottles of UV irradiated effluent in the clarifier of a wastewater treatment plant for one hour and found that the number of fecal and total coliforms increased by one logarithm. Bohm et al. (1982) put bottles of UV irradiated effluent in a waterbath in the sunlight and found that fecal and total coliforms increased in numbers by 1.4 to 1.7 logarithms. Fecal streptococci did not increase in numbers. Whitby et al. (1984) placed bottles of UV irradiated effluent in a clarifier for 6 hours and found that after 3 hours the fecal and total coliforms increased by a maximum of one logarithm. The fecal streptococci and Pseudomonas aeruginosa did not photoreactivate.

Harris et al. (1987b) studied photoreactivation in a wastewater which was disinfected with two different UV reactors. Samples of effluent were subjected to the light from a full-spectrum fluorescent lamp to encourage photoreactivation. After a quartz-sleeve and a teflon tube UV reactor the total coliforms increased by 2.0 and 0.5 logarithms respectively and the fecal coliforms increased by 1.5 and 0.5 logarithms respectively. There was little evidence of photoreactivation of fecal streptococci. In a laboratory study, Harris et al. (1987a) showed that E. coli and Streptococcus faecalis have the potential to photoreactivate and increase their numbers by 3.4 and 2.4 logarithms respectively.

Due to the potential for pathogenic organisms to photoreactivate, it has been suggested that photoreactivation be considered during the design of UV reactors and the setting of standards for ultraviolet disinfection.

This study used an antibiotic resistant E. coli which will photoreactivate to compare the degree of photoreactivation in vitro and in situ after the UV disinfection of wastewater.

METHOD

Project Site Description: The facility chosen for this study is located in Tillsonburg, Ontario, Canada. It is a conventional secondary treatment plant and receives primarily domestic wastewater.

Description of UV Unit: The system consists of a series of modules and each one has four UV lamps (13.8 W of light at a wavelength of 254 nm) enclosed in quartz sheaths. Two sets of ten modules for a total of 80 lamps were located in the effluent channel. The average flow over the lamps was $0.03m^3$/sec.

In-Situ Photoreactivation in the Receiving Stream: A nalidixic acid resistant (NAR) strain of E. coli was grown to approximately 9×10^7 cells per millilitre in 5 litres of trypticase soy broth containing 100 micrograms/mL of nalidixic acid. The broth culture was diluted with 45 litres of phosphate buffered water.

The cell suspension was transported on ice to the wastewater treatment plant in Tillsonburg.

The cell suspension was dispensed into the wastewater channel upstream of the UV disinfection unit at an approximate rate of one litre per second. An air diffuser system which was located in the channel bottom was used to distribute the bacteria as evenly as possible in advance of the UV unit. A 500 mL solution of fluorescein (200 g/L) was dispensed into the wastewater channel immediately after the cells of E. coli (NAR). This served as a marker for all of the downstream testing.

From previous dye tests, field personnel using stopwatches were able to take samples at precisely pre-determined times within the wastewater treatment plant and at the outfall into Big Otter Creek.

Personnel in a canoe followed the plume marked with fluorescein and took duplicate samples every half hour for two hours. Initial testing showed that the dye passed the plume of E. coli (NAR) almost immediately so that the sampling occurred behind the plume of fluorescein.

As the plume of E. coli (NAR) formed in the receiving stream a control sample was taken upstream from the point of discharge to determine the number of background nalidixic acid resistant E. coli.

Control runs were identical except that the number of cells of E. coli NAR were reduced to approximately 5 x 10^6 cells/mL. The suspension of cells was dispensed into the wastewater downstream from the UV unit.

One sampling site which was 20 to 30 minutes downstream from the outfall was used to determine the shape of the plume of E. coli (NAR). Samples were taken from ten minutes before the expected arrival of the plume until ten minutes after the arrival of the plume.

Samples were put on ice in the dark and returned to the laboratory for immediate microbiological analysis.

The membrane filtration technique was to used to enumerate E. coli (NAR). M-TEC agar was supplemented with 100 micrograms/mL of nalidixic acid (HAMES 1984).

The flow of Big Otter Creek was continuously monitored using automatic hydrograph stream gauging equipment.

The preceding experiments were repeated five times.

In-vitro Photoreactivation of E. coli (NAR)

Samples of the irradiated and non-irradiated *E. coli* (NAR) were taken in two litre beakers as the effluent discharged into Big Otter Creek. These samples were then dispensed into five sterile flint glass bottles and suspended on steel rods in the river. The bottles were 30 centimetres below the surface of the river. One sample was immediately put on ice to serve as the control. Bottles were removed every half hour for two hours.

This experiment was repeated five times and all of the analysis were identical to the previous section.

RESULTS

The shape of the plume of *E. coli* (NAR) in Big Otter Creek is shown in Figure 1. Consistent bacterial counts of *E. coli* (NAR) were obtained because the plume is very wide and the top of the curve is flat.

The flow rates of the river during the runs with irradiated and non-irradiated *E. coli* (NAR) were 4.16 m^3/sec. (SD=2.01) and 2.79 m^3/sec (SD=0.52) respectively. The flows for the two series of experiments (Figure 2) were very similar except for one of the runs with irradiated *E. coli* (NAR).

Figure 3 shows the levels of irradiated *E. coli* (NAR) in Big Otter Creek as the bacteria flowed down the river for two hours. No increase in the numbers of *E. coli* (NAR) was detected and the level continually declined.

Figure 4 illustrates the levels of non-irradiated *E. coli* (NAR) in Big Otter Creek as the bacteria flowed down the river for two hours. The numbers of *E. coli* (NAR) steadily declined during the two hours of sampling time.

Figure 5 shows the results of suspending irradiated and non-irradiated *E. coli* (NAR) in glass bottles in Big Otter Creek. During the two hour sampling period, the irradiated *E. coli* (NAR) increased by 1.9 times whereas the non-irradiated *E. coli* (NAR) decreased in numbers. A paired t-test showed that there was a significant difference in the numbers of irradiated *E. coli* (NAR) at 0 time and 2 hours. The level was significant at the 95% confidence interval.

DISCUSSION

When UV irradiated *E. coli* (NAR) was held in glass bottles and subjected to sunlight it underwent photoreactivation and increased in numbers by 1.9 times. This strain of *E. coli* shows a similar, although smaller response, to sunlight when compared to other studies where fecal coliforms were subjected to sunlight in glass bottles (Scheible and Bassell, 1981; Bohm *et al*, 1982; Whitby *et al*, 1984). In these studies the degree of photoreactivation of the fecal coliforms was about one logarithm whereas in this study *E. coli* (NAR) only increased by 0.28 logarithms. *E. coli* (NAR) has the ability to photoreactivate in a mixture of water from Big Otter Creek and the wastewater treatment plant. There was no increase in the number of non-irradiated *E. coli* (NAR).

The results of the *in situ* study of the photoreactivation of *E. coli* (NAR) are summarized in Figure 6. The decline in numbers of both the irradiated and control cells of *E. coli* (NAR) were identical. If photoreactivation had occurred, other factors such as sedimentation, dilution, predation and the naturally lethal effects of sunlight negated any increases in the number of bacteria. A similar effect is likely occurring with bacterial pathogens.

PART B: Bacteriophages as Indicators of Disinfection Efficiency of Wastewater

Bacterial indicator systems have proved to be useful for assessing the microbiological quality or safety of a wide variety of wastes (IAWPRC Study Group on Water Virology, 1983). Recent epidemiological and microbiological findings have raised serious concerns about the adequacy of fecal indicator bacteria for predicting the virological quality of water (Berg *et al*., 1978).

Ultraviolet light is being used to disinfect wastewater throughout North America and very little information is available about the relationship between indicator bacterial systems and pathogenic microorganisms especially viruses after UV disinfection.

Chang *et al.* (1985) found that the dose of UV light required to kill three logarithms of rotavirus and poliovirus was 3 to 4 times the amount of light to kill the same number of *E*. *coli*. *Salmonella*, *Shigella*, and *Staphylococcus* were equally sensitive to UV light. *Streptococcus faecalis* required about 1.4 times higher dose of UV light for the same degree of inactivation.

Harris *et al*. (1987) showed that poliovirus and reovirus required approximately 6 and 10 times the dose of *E*. *coli* for 99.9 % inactivation. Reovirus, a double-stranded RNA virus, was found to be significantly more resistant to UV radiation than poliovirus, a single stranded RNA virus.

Hill *et al*. (1970) contended that UV radiation can be highly effective and provide a reliable safety factor when treating estuarine water. They subjected four viruses to UV light and in increasing order of resistance they were: Poliovirus, Echovirus, Coxsachievirus and Reovirus.

Because viruses are more resistant to UV light than indicator bacteria, it is preferable to use an indicator organism which more closely resembles viruses. Bacteriophages may play a valuable role in this regard because they closely resemble the enteric viruses in structure, composition, morphology and size. The use of bacteriophages as indicators of water pollution has been suggested for many years (Hilton and Stotzky, 1973).

Replication of coliphages in water during the summer months (Vaughn and Metcalf, 1974) and the existence of many coliphages whose natural habitat appears to be the aquatic environment (Seeley and Primrose, 1980) prevents coliphages as a group from being ideal indicators of enteric viruses. Coliphages enumerated by *E. coli* represent a heterogeneous group of bacteriophages with various resistances to UV light and chlorine (Havelaar, 1986).

Havelaar and Hogeboom (1984) have developed a method for the enumeration of male-specific RNA bacteriophages in wastewater. These bacteriophages are very homogeneous in nature and their structure resembles the enteric viruses (Havelaar, 1986).

Havelaar and Nieuwstad (1985) found that F-specific bacteriophages were more resistant to chlorine in wastewater than thermotolerant coliforms and fecal streptococci.

Havelaar *et al*. (1986) used medium pressure mercury lamps and a shallow bed reactor to irradiate wastewater. The relative UV resistance of *E. coli*, fecal streptococci, somatic coliphages and F-specific bacteriophages were 1.0:1.5:1.1:2.3. They concluded that F-specific bacteriophages were suitable indicator organisms with regard to viral inactivation by UV light.

Using a batch UV reactor, Severin and Suidan (1985) found that at the 99.9% inactivation level an f2 bacterial virus (F-specific bacteriophage) was 6.8 times as resistant to UV light as *E. coli*. This would suggest that F-specific bacteriophage are as resistant to UV light as enteric viruses.

During this period of testing (Table 1) the chlorinated effluent did not meet the objective levels of 2500 total coliforms per 100 mL and 200 fecal coliforms per 100 mL whereas the UV effluent did.

Table 3 shows the results of the microbiological analysis of the F-specific RNA phages and somatic coliphages by the membrane filtration method and the normal indicator organisms along with P. aeruginosa before and after UV disinfection with and without photoreactivation. The results in Table 3 for all of the microorganisms is almost identical to the results in Table 1 for the same parameters. In this wastewater the MPN method and the MF method were equally as efficient at detecting the F-specific RNA bacteriophages but the MF method was more sensitive for the somatic coliphages after UV disinfection. The F-specific RNA bacteriophages and somatic coliphages were not affected by sunlight after UV disinfection. Bacteriophages do not undergo any repair process unless they are inside their respective host cell (Harm, 1980).

The total coliforms, fecal coliforms and E. coli underwent photoreactivation and increased by 1.2, 0.86 and 0.74 logarithms respectively.

The logarithmic survival of the F-specific RNA bacteriophages and somatic coliphages as measured by the MF method, the indicator organisms and P. aeruginosa after UV disinfection, with and without exposure to sunlight, are shown in Table 4. Except for P. aeruginosa which was detected in low numbers (Table3) all of the microorganisms are equally sensitive to UV disinfection and remain so after photoreactivation.

The results from the MPN and MF method for F-specific RNA bacteriophages and somatic coliphages differ from those of Havelaar et al. (1986). They found that F-specific bacteriophages were over twice as resistant to UV irradiation as E. coli and somatic coliphages. In this study E. coli, somatic coliphages and F-specific RNA phages were equally sensitive to UV light.

F-specific bacteriophages are not detected in appreciable numbers from humans but they are detected in wastewater in appreciable numbers (Havelaar _et_ _al_., 1986). Therefore Havelaar (1986) has suggested that F-specific phages should be used as a measure of disinfection efficiency and not as an indicator of human fecal contamination.

A study was undertaken to confirm the results of Havelaar _et_ _al_. (1986) who showed that F-specific bacteriophages were more resistant to UV light than _E_. _coli_.

METHODS

The F-specific RNA bacteriophages and somatic coliphages were measured before and after the disinfection of wastewater with UV light and chlorine.

The F-specific RNA bacteriophages and somatic coliphages were measured by two methods.

Membrane Filtration (MF) Method:

The MF method of Havelaar (1986) was used to measure the F-specific RNA bacteriophages. To measure the somatic coliphages the bacterial host was changed to _E_. _coli_ C and the broth and agar media was that of Scott _et_ _al_. (1979).

Most Probable Number (MPN) Method:

With the following changes the MPN method of Kott (1966) was used to measure the number of F-specific RNA bacteriophages and somatic coliphages.

When somatic coliphages were assayed the host was _E_. _coli_ C and the agar and broth media were that of Scott _et_ _al_. (1979).

When the F-specific RNA bacteriophages were enumerated the bacterial hosts and agar and broth media were that of Havelaar (1986).

The total coliforms, fecal coliforms, fecal streptococci, Pseudomonas aeruginosa and E. coli were measured by the membrane filtration method according to the Ontario Ministry of the Environment's Handbook of Analytical Methods for Environmental Samples (HAMES, 1984).

All of the UV irradiated samples were photoreactivated according to the method of Whitby et al. (1984). A second set was kept in the dark on ice as a control.

RESULTS AND DISCUSSION

Table 1 shows the results of the microbiological analysis of the indicator organisms and the F-specific RNA bacteriophages and somatic coliphages by the MPN method before and after UV irradiation and chlorination. The level of somatic coliphages was below the level of detection for the MPN method after UV irradiation. All of the measured parameters were much lower after UV irradiation than chlorination. This indicates that UV irradiation of this wastewater is much more efficient than chlorination.

Table 2 compares the logarithmic survival of the indicator organisms and the F-specific RNA bacteriophages and somatic bacteriophages as measured by MPN method. The logarithmic survival (log N/No) is the ratio of the number of microorganisms after disinfection to the number of microorganisms before disinfection. These results show that the microorganisms were much more resistant to chlorination than UV irradiation when the dose of chlorine was 1.45 mg/L and the free chlorine residual was 0.5 mg/L. All of the microorganisms except for the fecal streptococci appear to be equally sensitive (or resistant) to UV irradiation. The ratio of E. coli: fecal streptococci: fecal coliform: total coliform: F-specific RNA bacteriophages is 1:0.66:0.97:0.91:0.86. Similar results were observed for chlorination.

Havelaar and Nieuwstad (1985) found that both somatic coliphages and F-specific bacteriophages were more resistant to chlorination than the indicator bacteria in wastewater. F-specific bacteriophages were the most resistant. In this study the bacteriophages and indicator bacteria were almost equal in their sensitivity to chlorination.

Havelaar *et al*. (1986) stated that F-specific bacteriophages are suitable indicator organisms with regard to viral inactivation by UV irradiation. This study does not confirm this hypothesis because the F-specific bacteriophages were no more resistant to UV disinfection than the standard more easily enumerated indicator bacteria. The reasons for the difference between these two studies is not readily apparent.

Havelaar *et al*. (1986) used a shallow bed reactor which was similar to that used by Petrasek *et al*. (1980). Petrasek found that without baffles these systems have very poor turbulence and this may be important because the percent UV transmission in the study of Havelaar *et al*. (1986) varied from 24.4 to 57. Proper mixing is required so that all the microorganisms are subjected to an equal dose of UV light.

CONCLUSIONS

1. Although photoreactivation occurred with UV irradiated *E. coli* (NAR) in the receiving stream, other factors such as dilution, sedimentation, predation and the bactericidal effect of sunlight appear to negate any increase in the bacterial levels.

2. The photoreactivation of microorganisms may not be a major concern when wastewater is disinfected with UV light.

3. The normal bacterial indicators of the level of disinfection of wastewater were as resistant to UV light and chlorine as F-specific RNA bacteriophages which were proposed as an indicator of viral inactivation.

4. More detailed studies should be done to compare the resistance of enteric viruses and F-specific RNA bacteriophages in wastewater.

5. UV light was more efficient at disinfecting this wastewater than chlorine.

Table 1: The microbiological analysis of the indicator bacteria and the F-specific RNA bacteriophages and somatic coliphages by the MPN method.

Microorganism	Count/100 mL		
	Influent	UV Effluent	Cl_2 Effluent
F-specific RNA Phages	36,000	62	5,700
Somatic Coliphages	1,750	L* 1	140
Total Coliforms	108,000	130	13,600
Fecal Coliforms	25,000	19	1,600
Fecal Streptococci	1,800	13	725
E. coli	22,000	13	1,500

*Less than

Table 2: Logarithmic survival of the indicator bacteria and F-specific RNA bacteriophages and somatic coliphages as measured by the MPN method.

Microorganism	Log Survival	
	UV Effluent	Cl_2 Effluent
F-specific RNA Bacteriophages	-2.77	-0.80
Somatic Coliphages		-1.10
Total Coliforms	-2.92	-0.90
Fecal Coliforms	-3.12	-1.18
Fecal Streptococci	-2.14	-0.39
E. coli	-3.22	-1.15

A SPECIAL HYDROCYCLONE DESIGNED FOR SEWAGE TREATMENT

By

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Prepared for

Research Advisory Committee

Ontario Ministry of the Environment

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SUMMARY

There appears to be a valuable usage of hydrocyclones for removing from sewage the same types of particles they have been removing from paper pulp for the past 50 years. The recent development of a hydrocyclone which can be operated at low pressures, due to the recovery of the kinetic energy in fluid leaving the device, opens up new possibilities for use of hydrocyclones for sewage treatment. The project described in the attached report was to explore possible environmental application of the special hydrocyclone, by designing a unit for sewage treatment and testing its capability of removing particulate matter from sewage.

A report was written on the variables in design of a hydrocyclone and the probable results of changing them. After consultation with the Ministry it was decided that a unit should be built combining high capacity with fine particle separation. The final design choice was an energy recovery design with a 25 inch diameter cylindrical section and a 5 inch diameter exit of accepted fluid from the interior. Such a unit was constructed of mild steel and erected at Queen's University for testing and evaluation.

The test installation used a supply tank of 2 cubic meter volume with a stirrer to remix the rejected and accepted fluids which returned from the hydrocyclone. The hydrocyclone was fed by a 6 inch pipe line from a rubber lined pump. The inflow, reject flow and operating pressures were measured and samples taken of the feed, accepts and reject fluids for testing. These tests involved a wet screen analysis of the samples and microscopic examination of the resulting factors.

The hydrocyclone handled a flow of 37 liters/second at a pressure differential of 6 meters and was capable of removing 50% of grit particles 32 microns in diameter. Grit particles of 200 mesh particle size were removed completely and over 90% of grit particles 400 mesh in size were removed. Studies on removal of sawdust and coffee grounds indicated that the unit had roughly the same removal capability as for grit on particles with the same settling velocity in water. The unit removed virtually all grit from sewage and was efficient in removal of the larger dense granular particles. It was not very effective in removing

fibers, skins and fine organic particles.

There is little doubt that the hydrocyclone would be much more effective than existing devices in removing grit from sewage. Many particles which are presently removed by primary clarifiers could be removed by the hydrocyclone. The resultant impact upon the overall performance of a treatment plant and the performance of the secondary system is uncertain. This is however a new tool which may be useful to provide improved treatment of effluents.

Table 3: The microbiological analysis of the F-specific RNA bacteriophages and somatic coliphages by the MF method and the indicator bacteria after UV disinfection with and without photoreactivation.

		Count/100mL Effluent	
Microorganisms	Influent	No Photoreactivation	Photoreactivation
F-specific RNA Bacteriophages	23,000	130	170
Somatic Coliphages	430	3	2
Total Coliforms	130,000	170	2,500
Fecal Coliforms	32,000	40	290
Fecal Streptococci	1,600	8	16
P. aeruginosa	110	4	4
E. coli	22,000	34	190

Table 4: Logarithmic survival of the F-specific RNA bacteriophages and somatic coliphages as measured by the MF method and the indicator bacteria after UV disinfection with and without photoreactivation.

	Log Survival	
Microorganism	No Photoreactivation	Photoreactivation
F-specific RNA Bacteriophages	-2.20	-2.10
Somatic Coliphages	-2.10	-2.30
Total Coliforms	-2.90	-1.70
Fecal Coliforms	-2.90	-2.00
Fecal Streptococci	-2.30	-2.00
P. aeruginosa	-1.40	-1.40
E. coli	-2.80	-2.10

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THE EVALUATION OF NATIVE MARSH PLANT SPECIES FOR THE TREATMENT OF DOMESTIC SEWAGE

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Introduction

Treatment of domestic sewage by facultative lagoons is common practice for smaller communities in Ontario. As an alternative to traditional lagoon treatment, the Province of Ontario has conducted extensive research and demonstration projects to determine the advantages of utilizing emergent aquatic plants in artificial marshes as an alternative treatment of domestic sewage.

Marsh systems provide treatment of wastewaters by both physical and biological processes. Biological treatment is achieved by uptake of nutrients by the plant canopy and by decomposition of organics in a microbial community established on the roots, stems and hydrosol. Physical treatment processes includes precipitation, absorption, and floculation. Emergent plant species also have the unique ability to translocate oxygen to the root system, both in living plants and during the winter through hollow stem tissue. Oxygen released to the sediment and water column from plant rhizomes assists in maintaining an aerobic environment.

Initial investigations of marsh treatment systems were conducted at Listowel, Ontario, where lagoon effluent and aerated cell effluent was applied to various marsh system designs. Encouraging results from the

Listowel study led to the development in 1985 of a full scale, demonstration artificial marsh at Port Perry, Ontario. At both locations, the cattail (Typha angustifolia) was selected as the treatment species because it grows vigorously in monoculture stands and it is a common, native species readily available for planting. Early experimentation also suggested that this species was effective in treating wastewaters.

In addition to Ontario's two native species of cattail, two other emergent plants, Phragmites communis (Common Reed) and Scirpus validus (Soft Stem Bulrush), appear to meet the biological criteria necessary for successful marsh treatment. Both plants grow in dense monoculture stands, are native to Ontario and are capable of thriving in highly enriched aquatic environments. Research conducted principally in Europe indicates that Phragmites and Scirpus are effective at treating wastewaters in artifical marsh environment. However, there has been little investigation of the efficiency of Phragmites or Scirpus to treat domestic sewage in North America.

This study was initiated to evaluate these species through a direct comparison with narrow leaf cattail at the Port Perry sewage treatment facility. The study objectives are as follows:

1) To review and consolidate existing information on the use of these species for treatment of domestic sewage for waste treatment.

2) To establish identical small scale cells where a direct comparison of efficacy of treatment by three emergent plant species can be

undertaken.

3) To manipulate hydraulic and organic loading in the experimental system to determine optimum operating conditions and effluent quality throughout the year.

4) To develop cultural practice that would provide practical guidance to any future full scale use of a selected species.

5) To use the comparative data developed from the experimental plots within the full scale marsh to predict treatment capability in a full operating system.

During 1987, a supplementary substudy was incorporated into the research program. The primary objective of this substudy was to determine the effectiveness of a polishing cell supporting a floating cover of duckweed as a means to remove ammonia and phosphorus from marsh treatment system effluent.

The study extended over a two year period and was completed in the fall of 1987. For this reason, only preliminary results and conclusions are presented in this report.

Methods

The experimental marsh site was located adjacent to the existing demonstration marsh at Port Perry. Four steel cells were constructed, each 15m by 1.5m, providing a length to width ratio of 10:1. In the first year, monoculture stands of Phragmites, Typha, and Scirpus were established by transplanting root stock into three of the cells. The fourth cell served as a control cell. The four cells were loaded with a common influent. Figure 1 illustrates the physical layout of the experimental facility with the exception that the control cell is not shown.

Loading rates, water depths and theoretical retention times for Year 1 operation (August 1986 to February 1987) and Year 2 (May 1987 to October 1987) are given in Table 1. Water depth was controlled by standpipe height in each cell. For winter operation (November to May), all cell depths were adjusted to 30 cm, with corresponding retention times of 15 days.

Cell effluents were sampled twice monthly beginning in September 1987. Sample frequency was reduced to once a month beginning in November, and continued on a monthly basis during the winter. Bi-monthly sampling resumed in May, 1987. The study will continue through the fall of 1987 until the end of October, 1987.

Effluent samples from each cell were analysed for concentrations of BOD, suspended solids, total phosphorus, kjeldahl nitrogen and ammonia. Nitrate concentrations were determined for selected samples.

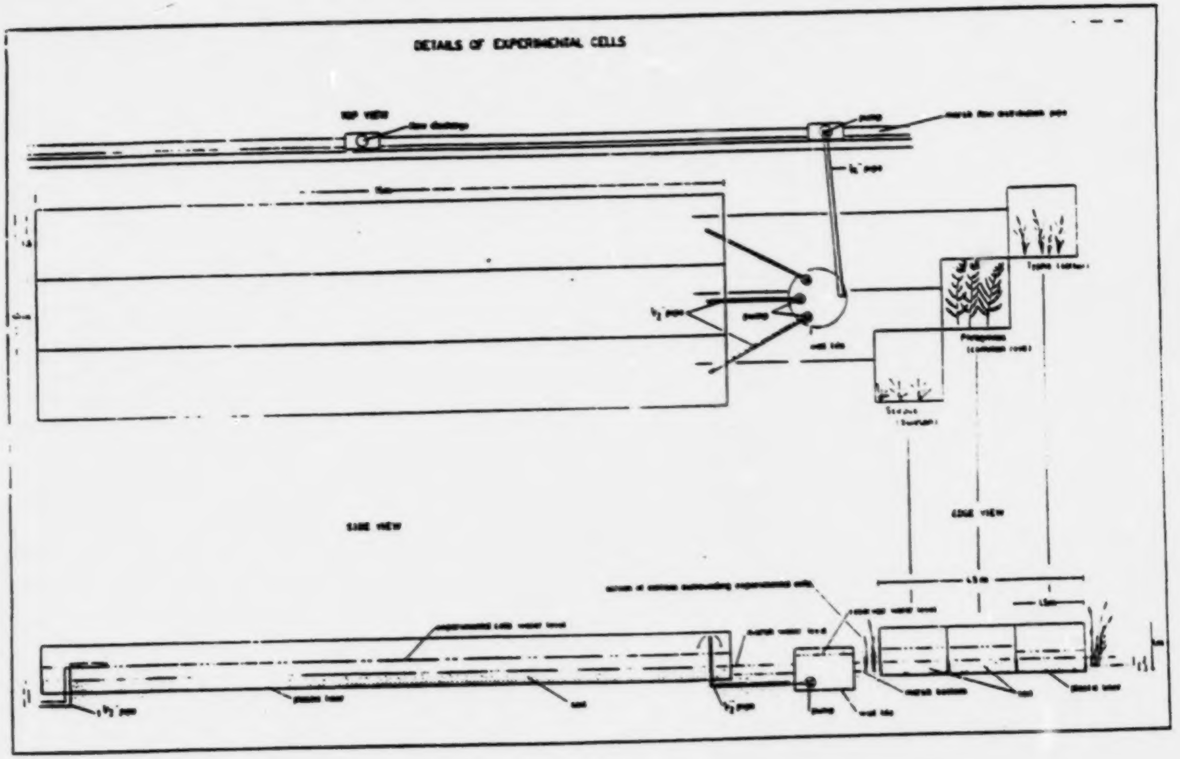
DETAILS OF EXPERIMENTAL CELLS
TOP VIEW
pump
SIDE VIEW
EDGE VIEW
Typha (cattail)
Phragmites (common reed)
Scirpus (bulrush)

Figure 1: Physical layout of experimental marsh facility located at Port Perry, Ontario to compare the capability of three emergent aquatic plant species (Phragmites communis, Typha angustifolia, and Scirpus validus) to treat domestic sewage. A fourth cell serving as a control is not shown.

Table 1: Loading rates, water depth, and theoretical retention times for experimental cells.

	Loading Rate (cubic meters/ha/day)	Water Depth (cm)	Retention Time (days)
1986			
Phragmites	200	10	5
Typha	200	20	10
Scirpus	200	30	15
Control cell	200	30	15
1987			
Phragmites	200	15*	7.5
Typha	200	15	7.5
Scirpus	200	30	15
Control Cell	200	15	7.5
Duckweed Polishing Cell**	600	15	2.5

* water depths adjusted July 7, 1987

** duckweed cell operational July 13, 1987

Concentrations of ammonia, dissolved oxygen and hydrogen sulfide were also determined with field test kits at the experimental site.

In the first year of operation, aeration cell effluent served as influent for the experimental marsh facility. The quality of aeration cell effluent was monitored regularly by the Ministry of the Environment. In the spring of 1987, decommissioning of the aeration cell precluded this source as an influent, and a mixture of raw sewage and lagoon effluent was used to provide a suitable influent. Sampling of the diluted, raw sewage influent was incorporated into the existing sampling program to monitor influent quality.

Initially, water depths were adjusted in each cell to depths that best suited the ecology of each species (Table 1). As part of the study program, water depths in each cell were adjusted to 15 cm in the second year to remove the effect of different retention times between cells. Also during July 1987, use of the fourth cell as a control was discontinued in order to establish a duckweed polishing cell. Effluent from the three plant cells was routed to a reservoir from which a mixed influent was pumped to the duckweed polishing experiment.

Influent and effluent of the duckweed polishing cell was sampled twice weekly and tested for concentrations of ammonia, dissolved oxygen and hydrogen sulfide with field test kits. Samples of influent and effluent were also collected in conjunction with the on-going sampling program for laboratory analysis. Operation parameters for the duckweed polishing cell are given in Table 1.

Duckweed was harvested regularly from the polishing cell to maintain a 75% or greater coverage and as a means to remove nutrients from the water column. The harvested duckweed was dewatered centrifugally using a hand operated salad spinner, and the wet mass determined. Samples of harvested duckweed were dried to determine percent moisture content, and representative samples frozen for subsequent determination of nitrogen, phosphorus and organic content by laboratory analysis. This information would be used to assess the potential of duckweed harvest as a means of nitrogen and phosphorus removal.

Results

Tables 2 and 3 give results to date of influent and effluent water quality data for the experimental cells and the duckweed substudy, respectively. Table 2 presents results of analysis from the 1986 summer period (September to October, 1986), the winter period (November 1986 to February 1987) and the 1987 summer period (May 1987 to November 1987).

Loading of the experimental facility began in the summer of 1986. Effluent sampling commenced in September. In the first year of operation, leakage in the control cell precluded filling of the control cell until November. In mid - February, the marsh facility completely froze, and winter sampling ceased at that point.

Startup of operations in the spring of 1987 was delayed until a new influent source was developed for the experimental marsh. Water depths in all cells were adjusted to 15 cm on July 7, 1987. The water depth in the *Scirpus* cell was restored to 30 cm following sampling on July 28 in an effort to halt an obvious dieback of *Scirpus* that was concurrent with the initial adjustment of water depth to 15 cm.

The results presented in Tables 2 are summarized below in terms of individual water quality parameters. Results of the duckweed polishing cell substudy are presented in Table 4 and summarized at the end of this section.

Biological Oxygen Demand (BOD)

All cells provided good reduction of BOD. Influent concentrations

Table 2: Experimental Cells Effluent Test Results - Average Values 1986-1987

Date		Summer, 1986	Winter, 1986-1987	Summer, 1987
Parameter				
BOD	Influent	15	15.4	52.9
(mg/L)	Phragmites	2.5	4.25	7.3
	Typha	1.5	6.25	9.1
	Scirpus	0.9	5.25	2.8
	Control	n/a	4.5	
S.S.	Influent	10.5	17.2	84.2
(mg/L)	Phragmites	7	15.5	24.9
	Typha	4.25	18.75	17.8
	Scirpus	2.75	16	11.7
	Control	n/a	22.3	
Ammonia	Influent	8.5	12.84	6.1
(mg/L)	Phragmites	1.9	8.8	0.71
	Typha	1.7	10.9	3.1
	Scirpus	0.61	8.9	1.8
	Control	n/a	9.6	
TKN	Influent	10.3	14	11.2
(mg/L)	Phragmites	1.69	11.1	1.82
	Typha	0.98	13.9	3.9
	Scirpus	0.71	11.1	2.7
	Control	n/a	11.4	
D.O.	Influent	5.1	9.9	3.8
(mg/L)	Phragmites	5	4.7	3.5
	Typha	3.3	2.9	1.84
	Scirpus	5.7	4.1	2.8
	Control	n/a	9.7	
Total P	Influent	0.53	0.54	2.7
(mg/L)	Phragmites	0.07	0.17	0.56
	Typha	0.1	0.17	0.85
	Scirpus	0.13	0.06	1.03
	Control	n/a	0.14	
H_2S	Influent	0	0	<.5
(mg/L)	Phragmites	0	0	0
	Typha	0	0	2.5
	Scirpus	0	0	0
	Control	n/a	0	

n/a - Data not available

Table 2: Experimental Cells Effluent Test Results - Average Values 1986-1987 (con't)

Date		Summer, 1986	Winter, 1986-1987	Summer, 1987
Parameter				
NO_3 (mg/L)	Influent			0.05
	Phragmites			0.03
	Typha			0.02
	Scirpus			0.04
	Control			
Fecal C.	Influent	16900	31000	2880000
	Phragmites	350	2260	10300
	Typha	11	1700	32700
	Scirpus	4	1550	3280
	Control	n/a	200	
Strepto.	Influent	1060	5400	84000
	Phragmites	160	330	11900
	Typha	52	930	46000
	Scirpus	72	370	2600
	Control	n/a	42	

n/a - Data not available

Table 3: Duckweed Polishing Cell - Water Quality and Biomass Harvesting Data -Average Results

Parameter	Ammonia (mg/L)	TP (mg/L)	DO (mg/L)	H_2S (mg/L)	BOD (mg/L)	S.S. (mg/L)	TKN (mg/L)	TP (mg/L)	NO_3 (mg/L)	Fecal Coliforms
Influent	2.7	2.14	2.5	0	3.2	57.7	2.1	0.87	0.035	5500
Effluent	0.68	0.62	8.4	0	1.8	40.7	1.16	0.41	0.03	870

were relatively low in the first year, averaging 15 mg/L, but averaged over 50 mg/L in the second year. Concentrations of BOD in cell effluents were normally below 10 mg/L. Treatment efficiency declined during the winter period.

Suspended Solids

Similar to BOD, concentrations of suspended solids in the influent increased from the first year to the second, averaging less than 20 mg/L in the first year, and more than 80 mg/L in the second. Treatment efficiency was good by all species, though treatment efficiency declined in the winter. Effluent concentrations of suspended solids normally remained below 20 mg/L.

Ammonia and TKN

Influent concentrations of ammonia ranged between 5 and 15 mg/L during both years. While all of the cells provided good reduction of ammonia, concentrations of ammonia in cell effluents increased during the winter. Similar to ammonia, good reductions of TKN were achieved during the summer, but declined during the winter period. Influent concentrations of TKN averaged between 10 and 15 mg/L during the study period.

Dissolved Oxygen and Hydrogen Sulfide

Dissolved oxygen concentrations in the influent averaged above 5mg/L in the first year and below 4 mg/L in the second year. Of the experimental cells, dissolved oxygen concentrations were usually lowest in effluent from the *Typha* cell. While no hydrogen sulfide was detected in cell effluents during the first year, hydrogen sulfide concentrations averaged 2.5 mg/L in effluent from the Typha cell during the second summer.

Total Phosphates (TP)

Influent concentrations of TP were approximately 0.5 mg/L in the first year, and averaged 2.7 mg/L in the second year. Concentrations of TP were reduced in all cells during both years of the study.

Nitrate

Selected samples of influent and effluents were analysed during the second summer for nitrate concentration. Effluent concentrations in the influent and cell effluents averaged below 0.05 mg/L.

Bacteria

Concentrations of bacteria (Fecal coliforms and Streptococcus) were reduced in all cells. Effluent from the Typha cell normally contained the highest concentrations of bacteria.

Results of the Duckweed Polishing Cell Substudy

Results presented in Table 3 indicate that significant reductions of ammonia were achieved by the polishing cell, although reductions in TKN were not as great. TP concentrations were reduced as well.

Further reductions in BOD were obtained by the polishing cell, however, reductions in suspended solids were not as pronounced. Dissolved oxygen concentrations were usually considerably higher in the effluent than influent, and the presence of hydrogen sulfide was not detected on any occasion in the effluent. Nitrate concentrations were below 0.1 mg/L in influent and effluent.

Regular harvest of duckweed and algae occurred through the study period, and on average, approximately 180 g/m^2 of fresh biomass was removed weekly.

Discussion

Development of thick, homogeneous stands of Phragmites and Scirpus during the study period indicates that these species, like cattails, can tolerate shallow, lagoon environments treating wastewaters of moderate strength. Over the two year period, no intrusion of one species into adjacent cells was observed, reflecting the ability of the experimental species to develop hardy stands capable of withstanding competition from other emergent species. Thus, where sufficient root stock was available, it would appear possible to establish large and stable treatment facilities with any of the three species evaluated.

Determining the environmental limitations of the experimental species was not a primary objective of this study. However, observations were made of environmental requirements which were considered important when considering the use of these species for wastewater treatment.

At different times during the study, raw sewage was accidentally or purposely applied to the cells. Both Scirpus and Phragmites reacted negatively to raw sewage inputs, and dieback of these species might have occurred if loading with raw sewage was continued. Reduced plant health was indicated by slumping plants and loss of colour and vigour in the leaves and stems. Typha, in comparison, appeared to suffer no negative effects from raw sewage loading. Indeed, the raw sewage supply employed during the second year of operation was directed to the Typha demonstration marsh, and overflow from the raw sewage supply standpipe into the demonstration marsh appeared to have little deleterious effects on surrounding cattails.

During the second season, water depth in the experimental cells was adjusted to 15cm, in order to provide equal retention times. A severe and rapid dieoff of Scirpus followed the depth adjustment. The dieoff should possibly have been anticipated, as Scirpus is best adapted to deeper waters, and requires support in the lower stem to maintain healthy growth.

The water depth was maintained at 15 cm in the Scirpus cell for four weeks, and at no time was their any indication of acclimation to the reduced depth. When the water depth in the Scirpus cell was re-adjusted to 30 cm, surviving plants returned to their original vigour relatively quickly.

While the depth change was greatest in the Scirpus cell (30cm to 15cm), Typha and Phragmites did not suffer any observable negative effects. This observation is perhaps most interesting in terms of Phragmites health, as Phragmites rarely occurs naturally where surface waters are continuously present.

Duckweed fully colonized the polishing cell shortly after the cell was filled in mid July, and regular harvest of healthy plants occurred for about two weeks before the plants paled and growth rate diminished. While the cause of the decline in duckweed vigour and growth rate is not fully understood, it is possible that excessive heating of leaf surfaces occurred during August. The walls of the polishing cell were painted black, and it is likely that significant heat energy was radiated to the upper leaf surface. A white netting material was subsequently used to reduce solar radiation (mesh size of approximately 1 cm), and which appeared to improve duckweed growth. Removal of the screen in early September further improved growth as air temperatures moderated.

Concurrent with the loss of duckweed vigour, an algae growth developed entraining the duckweed roots, which further reduced their growth rate during the mid summer period. Regular harvesting of algae and duckweed, and transplanting healthy duckweed to the polishing cell proved effective in controlling algae growth.

Conclusions

While this report is intended to be only preliminary, a number of general conclusions can be drawn at this time.

1) Good reductions in BOD and suspended solids concentrations were achieved by all species.

2) The experimental results indicate that both Phragmites and Scirpus may be more effective than Typha in treating domestic sewage, particulary in terms of hydrogen sulfide, ammonia, and bacteria reductions.

3) The loss of healthy growth of Scirpus in the second year resulting from reducing the water depth complicates interpretation of effluent data from that cell. In the first year, the Scirpus cell provided the best overall treatment of the experimental species.

4) Use of a duckweed polishing cell would appear to offer potential for removing ammonia and phosphorus from artificial marsh effluent.

A DEMONSTRATION STUDY FOR BIOLOGICAL PHOSPHORUS REMOVAL AT LAKEVIEW WPCP

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Introduction

Phosphorus removal in municipal wastewater treatment plants is usually achieved by conventional methods such as physicochemical precipitation with metal salts, including alum, ferric chloride and lime. While these methods have proven themselves reliable in reducing plant effluent total phosphorus concentrations to 1 mg/L and less, as effluent criteria become more demanding, the chemical costs increase dramatically.

The concept of biological phosphorus (bio-P) removal by activated sludge in excess of that required for normal cell metabolism was first reported in 1955[1]. The economic advantages of utilizing biological as opposed to physicochemical methods of phosphorus removal in the treatment of wastewater were immediately realized. These include a reduction in chemical costs for phosphorus removal, reduced aeration costs, and improved sludge handling.

Subsequent research has led to an increased understanding of the mechanisms involved and the development of several proprietary processes[2-6]. Many are commercially available and are marketed under trade names such as A/O, Bardenpho, Phostrip, UCT (University of Cape Town), and Phoredox. Figure 1 is an illustration of the flow diagrams for the various processes[7].

Each of these processes incorporates an anaerobic stage and an aerobic stage. The anaerobic stage involves a concurrent assimilation of organic matter and release of phosphate[8]. This is accomplished in the presence of polyphosphate (PolyP) organisms which have the ability to store polyphosphate in larger amounts than normally required for cellular functions[9]. Initially, the release and uptake of phosphates was attributed to the Acinetobacter strain of bacteria, but more recent research has indicated that other organisms, such as Aeromonas punctata also play in important role in the phenomenon[10].

The PolyP organisms convert the organic matter during the anaerobic stage to intermediate storage products, including poly-B-hydroxybutyrate (PHB) and at the same time release polyphosphates[11]. In the aerobic stage the stored PHB acts as an energy source for the synthesis of new cells during which time the released polyphosphates are accumulated in the new cells. The accumulation of polyphosphates in the aerobic stage is greater than its release in the anaerobic

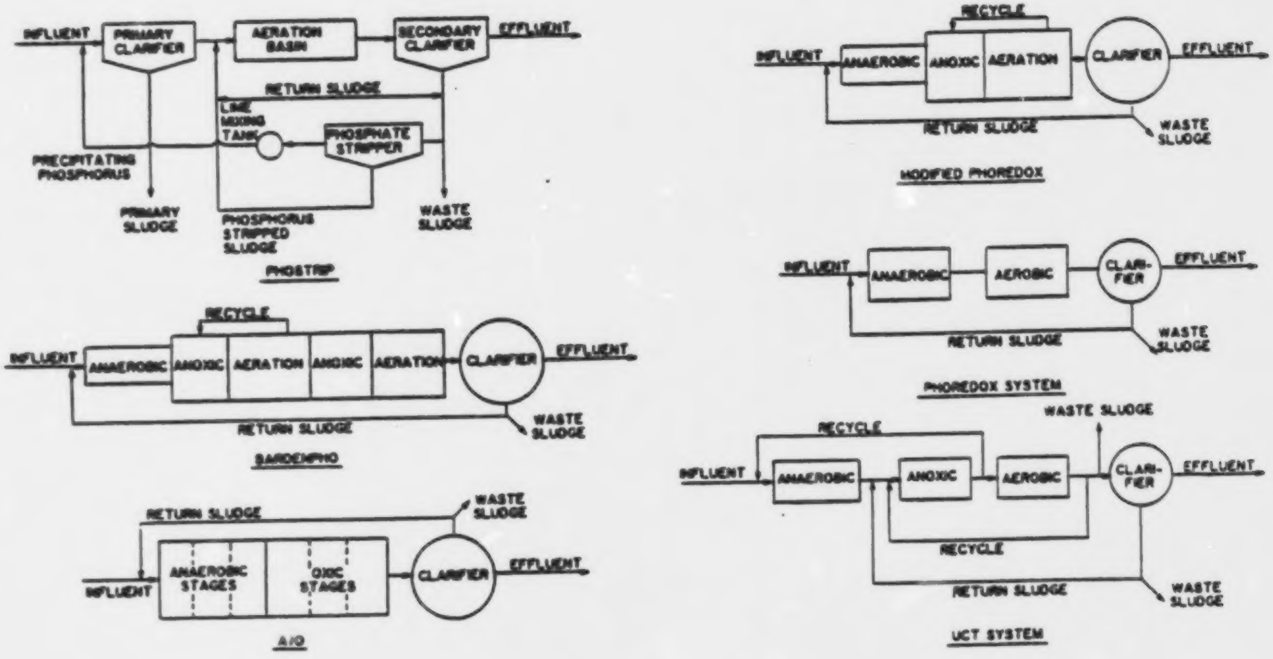

INFLUENT
PRIMARY CLARIFIER
AERATION BASIN
SECONDARY CLARIFIER
EFFLUENT
RETURN SLUDGE
LIME MIXING TANK
PHOSPHATE STRIPPER
PRECIPITATING PHOSPHORUS
PRIMARY SLUDGE
PHOSPHORUS STRIPPED SLUDGE
WASTE SLUDGE
PHOSTRIP
RECYCLE
INFLUENT
ANAEROBIC
ANOXIC
AERATION
ANOXIC
AERATION
CLARIFIER
EFFLUENT
RETURN SLUDGE
WASTE SLUDGE
BARDENPHO
RETURN SLUDGE
WASTE SLUDGE
INFLUENT
ANAEROBIC STAGES
OXIC STAGES
CLARIFIER
EFFLUENT
A/O
RECYCLE
INFLUENT
ANAEROBIC
ANOXIC
AERATION
CLARIFIER
EFFLUENT
RETURN SLUDGE
WASTE SLUDGE
MODIFIED PHOREDOX
INFLUENT
ANAEROBIC
AEROBIC
CLARI-FIER
EFFLUENT
RETURN SLUDGE
WASTE SLUDGE
PHOREDOX SYSTEM
WASTE SLUDGE
RECYCLE
INFLUENT
ANAEROBIC
ANOXIC
AEROBIC
CLARI-FIER
EFFLUENT
RECYCLE
RETURN SLUDGE
WASTE SLUDGE
UCT SYSTEM

FIGURE 1. FLOW DIAGRAMS OF VARIOUS BIOLOGICAL NUTRIENT REMOVAL PROCESSES

stage resulting in a sludge with a high phosphorus content[illegible]. The phosphorus is removed from the system by wasting a portion of the return sludge, as in a normal waste activated sludge system.

Several full-scale studies have been conducted on existing municipal wastewater activated sludge treatment plants to determine the feasibility of retrofitting them for bio-P removal[12,13]. Each retrofit situation, however, is site-specific and a plant should be given individual consideration in terms of wastewater characteristics, operational difficulty, and cost effectiveness before a retrofit is implemented.

The Lakeview Water Pollution Control Plant (WPCP) in Mississauga, Ontario currently achieves phosphorus removal by precipitation with ferric chloride. An assessment of the wastewater to the plant indicated that it met the requirements for a bio-P removal retrofit[7]. On this basis, the plant was chosen as the site for a full-scale demonstration study. The objectives of the three phase study were to demonstrate the benefits of bio-P removal in a full-scale operation.

Phase 1 was an operation of the test aeration tank without chemical addition to purge the residual iron from the system and provide a sludge for biological phosphorus removal. Phase 2 involved the introduction of an anoxic zone in the first pass of the test aeration tank. It examined the effect of minimum air supply in the removal of phosphorus and system operation. Phase 3 involves the introduction of an anaerobic zone in the test aeration tanks to examine biological phosphorus removal efficiency.

This report focuses on the third phase of the study which was designed to assess the potential reduction in chemical precipitant dosage while still achieving a high level of phosphorus removal, and possible savings in overall power costs, while identifying any operational difficulties resulting from the process modifications.

Materials and Methods

Lakeview Water Pollution Control Plant

The Lakeview WPCP is located in the south east portion of the City of Mississauga. The Plant was initially constructed in 1961 with a design capacity of 22,500 m^3/d. An extension in 1967 increased this capacity to 56,000 m^3/d. In 1968 a plan for the control of water pollution in South Peel was established in which the Lakeview and Clarkson plants were designated to serve the east and west sections of South Peel, respectively. The plant capacity was subsequently expanded to 168,000 m^3/d in 1972. A third plant was added in 1975 which brought the total facility capacity up to its present value of 280,000 m^3/d.

Figure 2 is a process flow schematic of the Lakeview WPCP. The wastewater undergoes primary and secondary treatment including screening and grit removal, primary settling, aeration, final settling, chemical phosphorus removal and disinfection prior to discharge to Lake Ontario. The secondary sludge undergoes thickening after which it is combined with the primary sludge and sludge from the Clarkson plant. The sludge is subject to thermal conditioning and dewatering prior to incineration. Sidestreams from the thermal conditioning unit and the dewatering facility are anaerobically treated in Hyan reactors and recycled to the plant headworks along with centrate from the centrifuge sludge thickeners.

An average effluent phosphorus concentration of 1 mg/L is presently achieved at the Lakeview WPCP by precipitation with ferric chloride. A ferric chloride solution is added to the activated sludge secondary treatment sections. The aeration tanks are of three pass tanks equipped with coarse bubble diffusers along one side to provide a spiral flow pattern.

Plant Modifications for Biological Phosphorus Demonstration

The bio-P demonstration was conducted in the first plant (system 1) and its expansion module (system 2) as shown in Figure 3. System 1 consists of two equally sized aeration tanks (No. 1 and No. 2) and four final settling tanks (Final 1-4). System 2 consists of two equally sized aeration tanks (No. 3 and No. 4) and two final clarifiers (Final 5 and Final 6). Each system has a

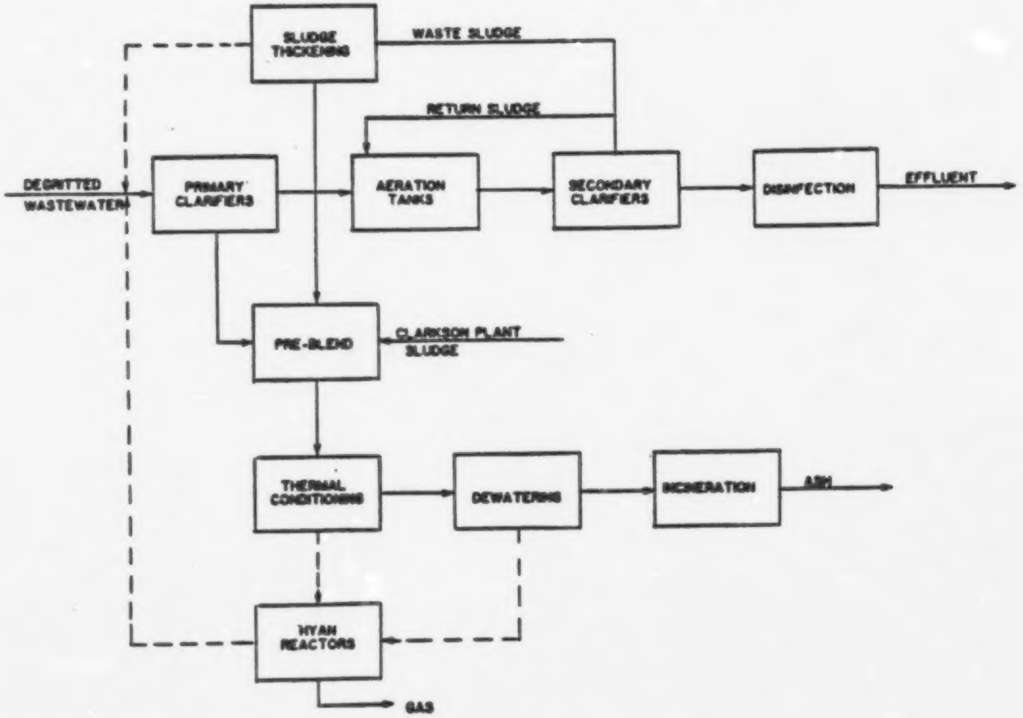

SLUDGE THICKENING
WASTE SLUDGE
RETURN SLUDGE
DEGRITTED WASTEWATER
PRIMARY CLARIFIERS
AERATION TANKS
SECONDARY CLARIFIERS
DISINFECTION
EFFLUENT
PRE-BLEND
CLARKSON PLANT SLUDGE
THERMAL CONDITIONING
DEWATERING
INCINERATION
ASH
HYAN REACTORS
GAS

FIGURE 2. PROCESS FLOW SCHEMATIC
LAKEVIEW WPCP

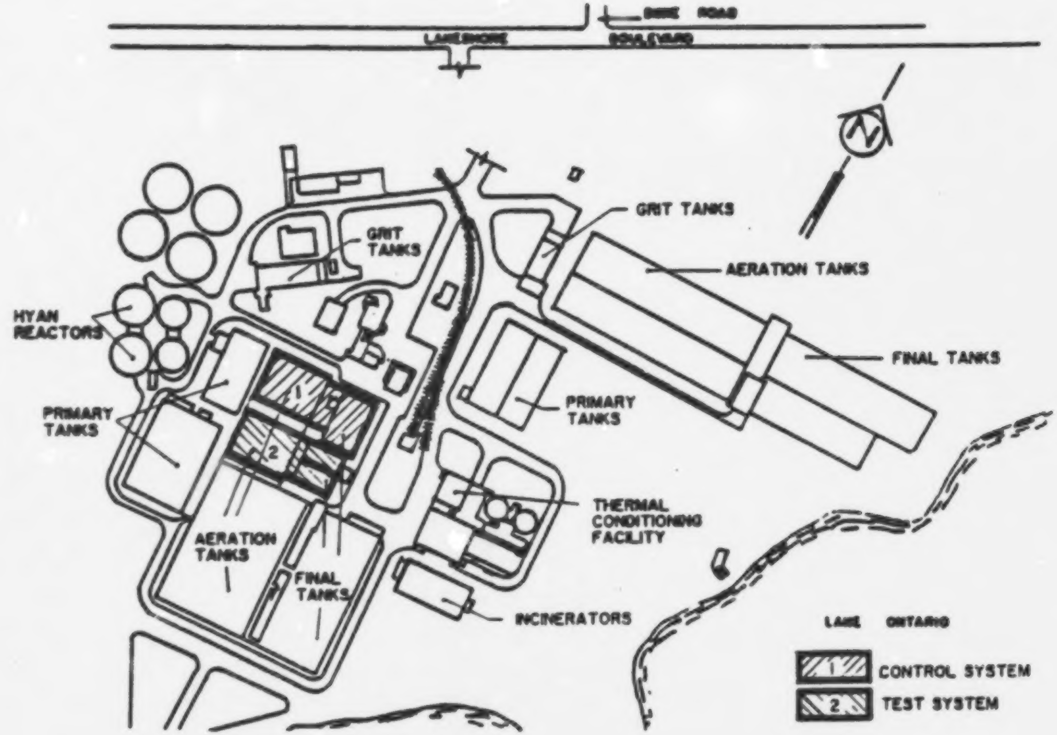

DIXIE ROAD
LAKESHORE BOULEVARD
GRIT TANKS
AERATION TANKS
FINAL TANKS
GRIT TANKS
HYAN REACTORS
PRIMARY TANKS
PRIMARY TANKS
THERMAL CONDITIONING FACILITY
AERATION TANKS
FINAL TANKS
INCINERATORS
LAKE ONTARIO
1
2
1 CONTROL SYSTEM
2 TEST SYSTEM

FIGURE 3. LAKEVIEW WATER POLLUTION CONTROL PLANT

separate return sludge facility. Both systems receive their feed from the same primary effluent channel. System 1 was operated normally as a control unit and System 2 used for the demonstration.

The capacity of each system is approximately 28,400 m^3/d (6.25 MGD), or about 13% of the total plant capacity. In the event of operational failure of the bio-P demonstration system, the impact of the test-system effluent on the overall plant effluent quality would not have been significant. The design parameters of the systems are shown in Table 1.

Table 1 Design Parameters of Control and Test Systems

Component	Design Parameters System 1 (Control)	System 2 (Test)
Aeration Tanks		
Number of tanks	2	2
Total tank volume (m^3)	7,200	6,900
Final Settling Tanks		
Number of tanks	4	2
Tank area (m^2)	1,126	966
Tank volume (m^3)	3,770	3,540
Weir length (m)	284	338

An anaerobic zone was introduced in the first pass of the aeration tanks of the demonstration system by shutting off the air supply. Mixing was maintained in the tanks through the installation of three 5.6 kw mixers. Due to the fact that there were only three mixers available, the two aeration tanks in the bio-P demonstration system were operated with different configurations. Aeration Tank No. 3 had two mixers in the first two-thirds of the first pass while Aeration Tank No. 4 had one mixer placed in the first one-third of the first pass. The aeration was reduced to provide a liquid velocity of approximately 0.3 m/s in the next one-third to prevent any solids from settling. The return sludge from the two demonstration tanks could not be separated, however, and was consequently returned to both tanks via a common line.

Sampling and Analysis

The influent and effluent for the control and demonstration systems were analyzed for the study. Because the operating configuration of the two aeration tanks of the demonstration system were not identical, they were monitored individually. Samples were 24-hour composite except as indicated. The parameters monitored, sampling locations, and weekly sampling frequency are listed in Table 2.

Table 2 Parameters Monitored, Sampling Locations and Weekly Sampling Frequency for Bio-P Demonstration

Parameter	Sampling Points and Weekly Frequency						
	Primary	Aeration Tanks			Final Settling Tanks		
	Effluent	1 - 2	3	4	1 - 4	5	6
Flow	4				4	4	4
BOD_t	4				4	4	4
BOD_s	4				4	4	4
SS	4				4	4	4
P_t	4				4	4	4
P_s	4				4	4	4
Recycle Flow		4	4	4			
MLSS		4	4	4			
MLVSS*		1	1	1			
Waste Sludge Flow		4	4	4			
Waste Sludge Solids*		4	4	4			
SVI		4	4	4			

* Grab samples

In addition to those parameters shown, samples were taken of the primary influent, mixed liquor, and final effluent and analyzed for iron. This was done to determine the iron recycled in the system through the various process sidestreams and to assess the degree of bio-P removal.

All analyses were performed according to Standard Methods[14]. Iron samples were analyzed on a Varian SpectrAA - 20.

Results and Discussion

Phase 1 and Phase 2

The bio-P demonstration consisted of three phases. Phase 1 and 2 were conducted only on the expansion module of the first plant with one aeration tank serving as a test train and the other serving as the control train. Phase 1 was simply an operation of the test train without chemical addition in order to purge the residual iron from the system and provide a sludge conducive to bio-P removal. It was found, however, that even after the addition of ferric chloride to the test train was discontinued for four months, the concentration of iron was still high, approximately 21 mg Fe/g SS in the mixed liquor. Analysis of the raw wastewater, centrate, HYAN reactor effluent, primary influent, and primary effluent revealed that most of iron in the primary effluent was from the recycle of centrate and HYAN reactor effluent. These sources accounted for approximately 50% of the total iron in the system. The two recycle streams, however, could not be diverted due to prohibitive costs.

Phase 2 of the demonstration was designed to examine the effect of an anoxic zone in the first pass of the test aeration tank on phosphorus removal. The aeration tanks are spiral flow, three pass tanks with diffusers located on one side. During normal operation, the air supply to the tanks for the mixing and oxygen requirements is capable of creating a spiral flow velocity of 1.2 to 1.8 m/s at the tank floor. For the demonstration, the air supply to the entire first pass was reduced to maintain a spiral flow velocity of approximately 0.45 m/s. At this velocity, the dissolved oxygen in the first pass was measured to be 0 mg/L.

For the first 35 days of Phase 2 the test train was operated without chemical addition for phosphorus removal. The effluent phosphorus concentration during this time averaged 2.6 mg/L, a reduction of 59% of the influent value of 6.4 mg/L. The aeration tank operating with only an anoxic zone was not capable of providing an effluent suitable for discharge and chemical addition was resumed in the second portion of Phase 2.

The test train was operated for periods of 19 days and 16 days at iron doses of 1.5 mg Fe/L and 3.0 mg Fe/L, respectively. At a dose of 3.0 mg Fe/L, the test train produced an effluent with an average phosphorus concentration of 1.09 mg/L while the control train produced an effluent with an average phosphorus concentration of 1.07 mg/L at its normal dose of about 10 mg Fe/L. In effect, the test train achieved the same effluent phosphorus concentration with 70% less chemical addition.

Phase 3

As mentioned previously, in the third phase of the demonstration study, both the first plant and its expansion module were used and operated as a control system and a test system respectively. Addition of chemical precipitant (FeCl) was discontinued in the test system. To ensure that the control and test systems were operating under otherwise comparable conditions, the operating parameters for the aeration tanks and final clarifiers were monitored. The average values for these parameters are listed in Table 3. It should be noted that Aeration Tank No. 4 was taken out of service for repair to Final Clarifier No. 6 at day 38 of the study and the values presented reflect the performance of the tank until that point.

Table 3 Average Operating Parameters of Control and Test Systems

	Control System	Test System	
	A.T. 1 & 2	A.T. 3	A.T. 4
Average Flow (m^3/d)	24,740	11,250	12,430
Aeration			
Detention Time (hrs.)	7.16	7.46	6.72
Organic Load (kg BOD/m^3.d)	0.64	0.64	0.74
MLSS	3,026	2,729	3,256
F/M	0.25	0.29	0.39
SVI	83.0	82.7	86.2
Final Settling	Final 1-4	Final 5	Final 6
Detention Time (hrs.)	3.85	3.82	3.54
Surface Overflow (m^3/m^2.d)	23.91	23.91	25.73
Weir Overflow (m^3/m.d)	87.09	68.26	73.48

Throughout the study, the operation of the control and test systems was examined to determine whether the bio-P demonstration systems exhibited any operational difficulty. After day 36 of the study it was observed that some odour could be detected in Aeration Tank No. 3. By day 38 the operating configuration of the

Aeration Tank No. 3 was changed to that of the Aeration Tank No. 4. (One mixer in the first one-third of the first pass and reduced air flow to the next one-third.) This was the same day that the Aeration Tank No. 4 was taken out of service for repair to the final clarifier sludge collector.

The sludge volume indexes during the study for the control and test tanks are shown in Figure 4. With the exception of two high values for aeration tank No. 4, the SVI's recorded for the test tanks were generally below 120 and comparable to the control section. The high values were recorded within the first 10 days of the study and can be attributed to a period of acclimation. No problems were encountered with the final clarifier operation of the test tanks in terms of sludge bulking.

The mixed liquor suspended solids shown in Figure 5 are more variable, particularly for the test tanks. However, the average MLSS values and F/M ratios shown in Table 3 indicate that the overall loading on the aeration tanks was similar. The average F/M for aeration tank No. 4 was slightly higher because it was taken out of service during a high flow period.

Similar levels of treatment were obtained with the control and test tanks. This is illustrated in Figures 6 through 8 which depict the effluent BOD, SS, and P trends for the duration of the study. The average values for these parameters are listed in Table 4.

Table 4
Average Effluent Parameters

Parameter	Control System Final 1 - 4	Test System Final 5	 Final 6
BOD	25.2	17.5	17.2
SS	21.5	14.6	23.3
P	0.9	1.0	0.6

While a fluctuation in the effluent quality can be expected in any biological system, there were several incidents which contributed to the variation seen in Figures 6 to 8. On day 17 of the study a break in a sewer line near the Etobicoke Creek resulted in increased flow through infiltration to the entire plant. At the same time, a final clarifier in another section of the plant was taken out of service for repair. A portion of the flow from this section had to

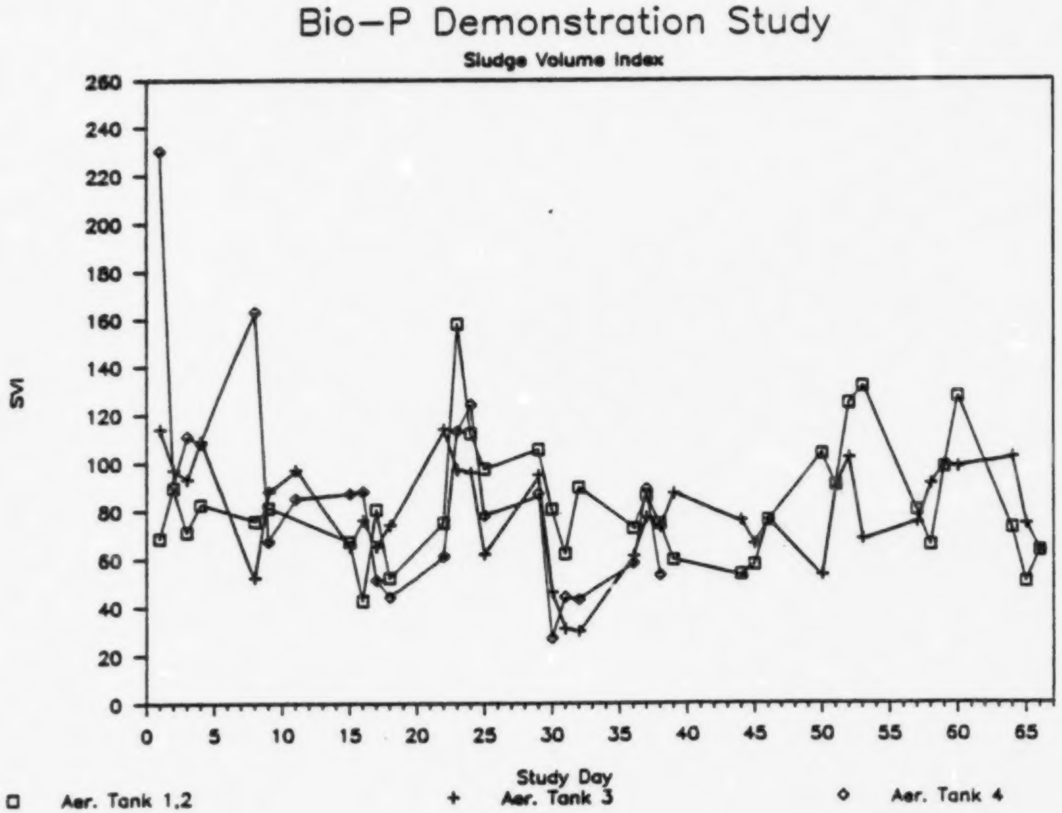

Bio-P Demonstration Study
Sludge Volume Index
SVI
260
240
220
200
180
160
140
120
100
80
60
40
20
0
0
5
10
15
20
25
30
35
40
45
50
55
60
65
Study Day
□ Aer. Tank 1,2
+ Aer. Tank 3
◇ Aer. Tank 4

FIGURE 4

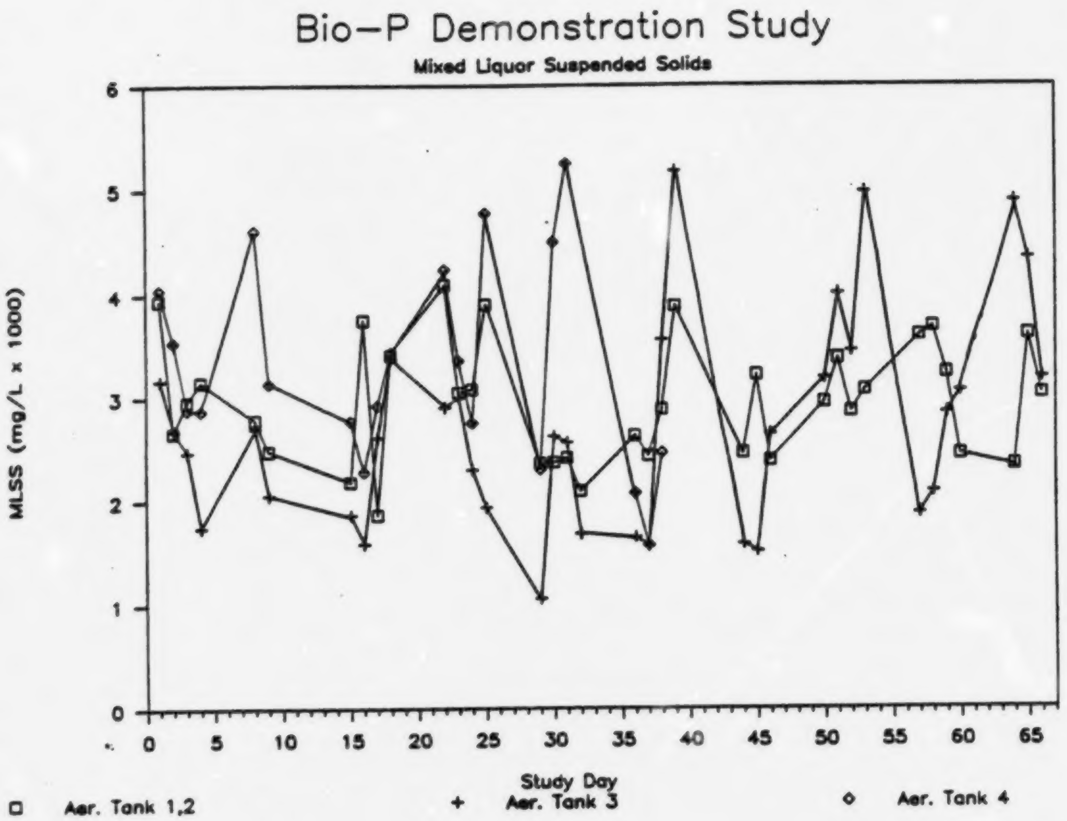
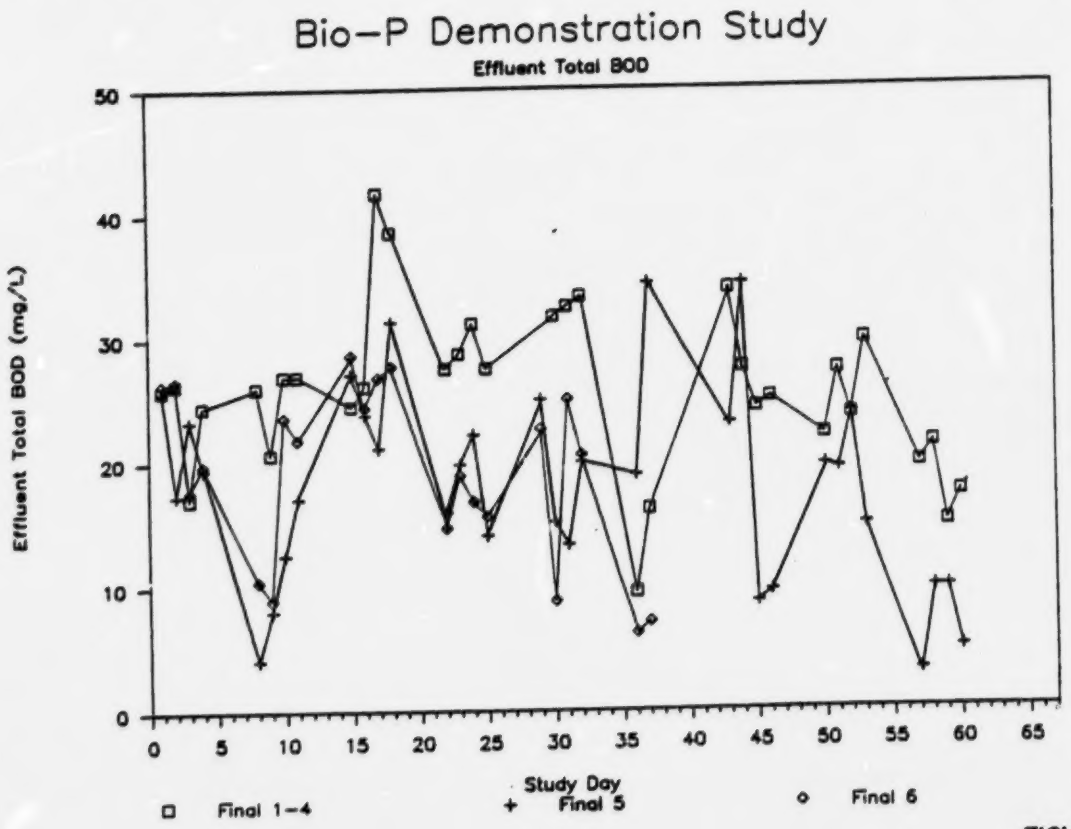

Bio-P Demonstration Study
Mixed Liquor Suspended Solids
MLSS (mg/L x 1000)
0
1
2
3
4
5
6
0
5
10
15
20
25
30
35
40
45
50
55
60
65
Study Day
□ Aer. Tank 1,2
+ Aer. Tank 3
◇ Aer. Tank 4

FIGURE 5



Bio–P Demonstration Study

Effluent Total BOD

FIGURE 6

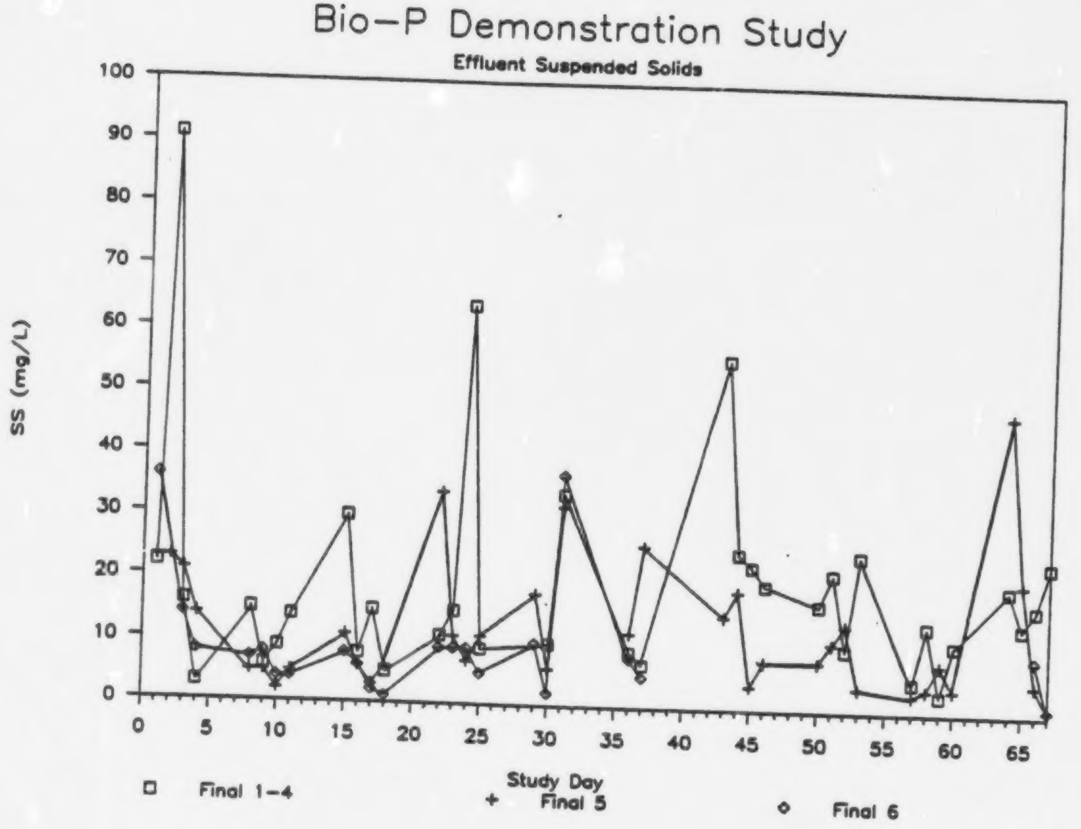
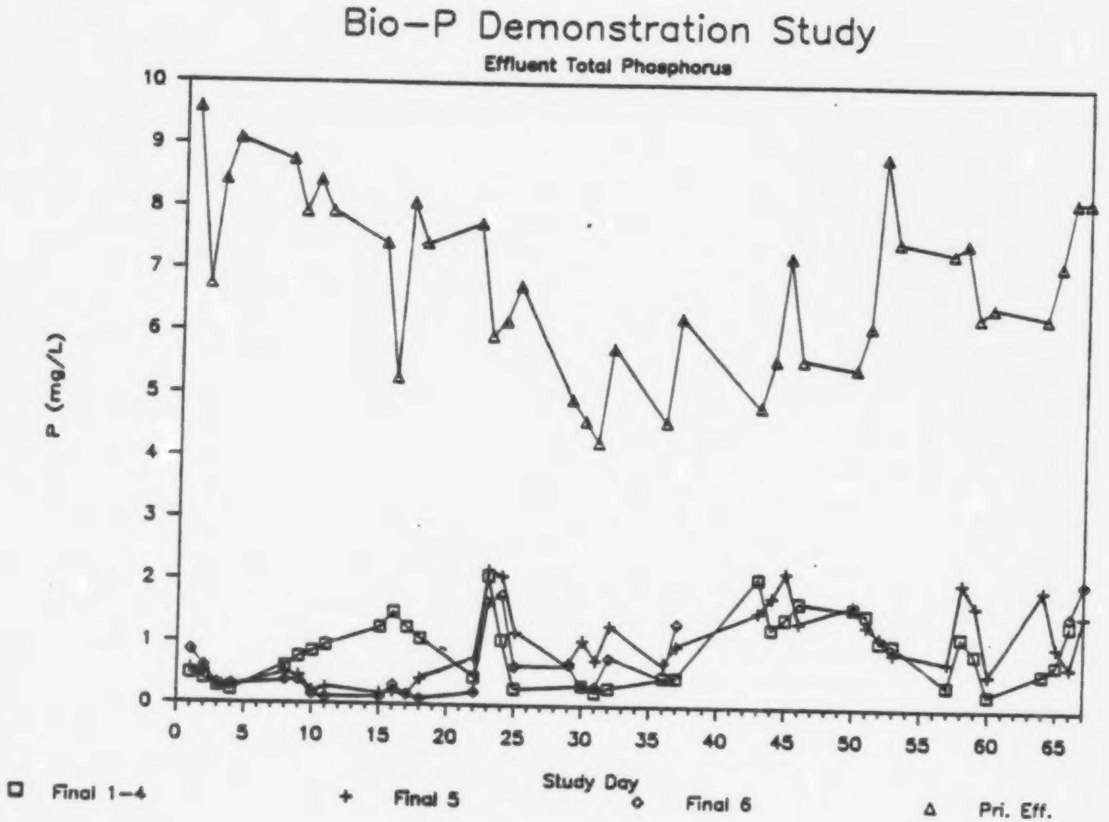

Bio-P Demonstration Study
Effluent Suspended Solids
SS (mg/L)
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
35
40
45
50
55
60
65
Study Day
Final 1-4
Final 5
Final 6

FIGURE 7


Bio-P Demonstration Study

Effluent Total Phosphorus

FIGURE 8

be directed towards the first plant and its expansion module. An immediate rise in the effluent BOD concentration can be seen in Figure 6 on the second day after this occurrence. Similarly, the effluent SS and P concentrations jumped, although this took an additional two days to become evident. The sewer line was repaired by day 24 and the final clarifier was put back into service on day 26. A reduction in all three of the parameters monitored is apparent at day 28 of Figures 6 to 8.

Discharges from nearby industries were observed to enter the plant on several occasions. Specifically, these discharges were recorded on days 10, 18 to 20, 27, 39 and 44 of the study. The impact on the plant performance was apparent once the flow was reduced to normal levels. The discharge on day 39 is followed by an increase in the plant effluent parameters on day 43. After a short period of stabilization, the discharge of day 44 can be identified by another increase in the effluent parameters.

In all three cases there was some excedence of the effluent requirements imposed by the Ontario Ministry of the Environment. However, the average effluent P concentration for both sections did meet the Ministry criterion of 1 mg P/L or less.

The results of Phase 1 of the study had indicated that there were large concentrations of residual iron entering the system through the Hyan effluent and sludge thickener sidestream. To determine the concentration of iron entering and leaving the Bio-P systems, iron samples were taken of the raw sewage, primary effluent and the effluent from each system. The results of the analyses on these samples are shown in Table 5.

Table 5
Iron Concentration in Bio-P
Demonstration Systems

Sampling Location	Fe Concentration (mg/L)
Raw Sewage	4.4
Primary Effluent	7.7
Final 1 - 4	1.2
Final 5	0.52
Final 6	0.39

As expected, the iron concentration in the primary effluent was significantly higher than in the raw sewage. This raised the question of whether the low phosphorus levels witnessed in the test system were a result of biological uptake or preciptation with the recycled iron in the system.

Previous research demonstrated that phosphorus that is precipitated with metal salts is not released under anaerobic conditions[15]. Conversely, phosphorus that has been assimilated for cellular metabolism is released in soluble form. A test program was initiated to determine if the phosphorus in the sludge of the test section was organically or inorganically bound.

Grab samples were taken of the return sludge from System 1 and System 2. The samples were analyzed for suspended solids, iron, total and soluble phosphorus. They were then capped and allowed to go septic over a 5 day period. After this time the samples were once again analyzed for soluble phosphorus to measure the quantity released under anaerobic conditions. The average values for these analyses are listed in Table 6.

Table 6
Anaerobic Phosphorus Release Tests

Parameter	Aeration Tanks 1, 2	Aeration Tanks 3, 4
% VSS	66.7	77.25
VSS (mg/L)	5,572 (5.830)	4,639 (5.110)
mg Fe/g VSS	165.7 (165.7)	47.4 (35.8)
mg P/g VSS	49.9 (38.6)	49.3 (31.3)
mg P released/g VSS	0.8 (0.3)	5.9 (12.9)
% P released	1.7 (0.8)	13.8 (43.5)

In each case, the amount of soluble phosphorus released by the bio-P demonstration section sludge was greater than that released by the control section sludge. On average, this was 13.8% as compared to 1.7%. The numbers in parenthesis are values obtained for one of the pairs of samples which was allowed to remain under anaerobic conditions for an additional 7 days. In this particular case, a much larger quantity of phosphorus was released by the sludge in the test tanks - 43.5% as compared to 0.8%.

The iron concentration in the control section sludge was greater than that in the bio-P demonstration section, as would be expected. The average concentration of iron in the control section was 165.7 mg Fe/g VSS and 47.4 mg Fe/g VSS in the demonstration section. The relatively high value for the demonstration section can be attributed to the recycled flows from the previously mentioned process sidestreams. This iron, however, did not have any demonstrable effect on the fate of the phosphorus as was shown by the release of phosphorus under anaerobic conditions. It should be noted that the volatile content of the test tank sludge was significantly higher than that of the control system because of the reduced iron concentration.

Under normal operating conditions, an iron dose of 10 mg Fe/L to the influent is maintained at the Lakeview Plant. The addition of iron to the control system was monitored for the duration of the study. In this time approximately 19,500 kg of iron were added to the control system. Based upon a unit cost of $0.209/kg Fe, this resulted in a total cost of $4,080 or $60.87 per day.

The addition of iron cannot be discontinued completely at the Lakeview plant because, as with any biological system, upsets are likely to occur. However, if it is assumed that a concentration of 3 mg Fe/L is sufficient to maintain the required effluent phosphorus concentration of 1 mg/L (as was demonstrated in Phase 2 of the study), a 70% saving in chemical cost may be realized. In terms of the entire Lakeview plant flow, this represents an annual saving of approximately $70,000.

An average increase of 35% in sludge volume may be expected in secondary plants which employ metal salts for phosphorus removal[14]. The quantity of sludge wasted from System 1 and System 2 was monitored during the demonstration to see if there was a reduction in sludge production. The monitoring program revealed that, on average, $577.7 m^3/d$ were wasted from the control system as compared to $494.9 m^3/d$ from the test section, a difference of 17%.

The savings in aeration costs could not be quantified at the time of writing. However, it is believed that a significant reduction in power consumption can be realized. This will be confirmed through the measurement of air flow to the two systems.

Conclusions

The following conclusions have been drawn from the results of this study:

1. The wastewater characteristics at the Lakeview WPCP are suitable for the implementation of bio-P removal.
2. Implementation of a bio-P removal retrofit in the first plant and its expansion module of the Lakeview WPCP did not result in any operational difficulties which could not be corrected.
3. Effluent quality at the Lakeview WPCP did not suffer because of the implementation of bio-P removal.
4. Substantial savings in chemical costs can be achieved through the implementation of bio-P removal.

Recommendations for Further Study

This study has demonstrated that, given the characteristics of the influent wastewater at the Lakeview WPCP, bio-P removal is possible through the introduction of an anaerobic zone in the aeration tanks. For the process modification to be implemented as a part of the regular plant operation, however, further study is required. In particular, the effect of the sludge handling scheme on bio-P sludge must be assessed. Care must be taken to ensure that the biologically bound phosphorus is removed completely from the system rather than released during thermal conditioning and recycled via a process sidestream.

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B18 TOWNSHIP OF IGNACE, VYREDOX TREATMENT PLANT FOR A GROUNDWATER SUPPLY.

D.R. Turnbull and J. A. Harris,
International Water Supply Ltd.,
Barrie, Ontario.

Not available in time for printing.

OPTSTOR COMPUTER PROGRAM FOR COST-EFFECTIVE STORAGE IN SEWER SYSTEMS

Sheldon H. Zemell* and Rob Bishop**

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**Marshall Macklin Monaghan Limited, Don Mills, Ontario

ABSTRACT

Nearly ten years ago, OPTSTOR was originally developed by MacLaren as a tool for determining cost-effective locations and volumes for storage in a surcharged sewer system. In the current project begun at the start of this year, OPTSTOR has been upgraded significantly in several respects. The program has been generalized to include not only local off-line storage, but also trunk off-line, trunk in-line and local in-line storage. In addition, the efficiency, user interface and program documentation have been markedly improved.

OPTSTOR is used together with the U.S. EPA SWMM model. The RUNOFF Block of SWMM serves to generate estimates of inflows, while the EXTRAN Block simulates the time-dependent hydraulic status of the system to provide the downstream head. Then, the steady-state OPTSTOR program is applied to individual lines within the network to determine storage requirements.

In OPTSTOR, hydraulic losses are described by the Manning Formula (as in EXTRAN). For each of the four types of storage considered, curves relating the volume required for any given percentage reduction in peak flow have been derived and are embedded in the program. The cost is taken to be a bilinear function of storage volume.

The minimization of storage costs is achieved by means of the so-called Complex Method due to M.J. Box. An initial complex of feasible solutions is obtained. Then, these are improved by means of "reflections" of the current maximum-cost solution about the centroid or reduced centroid of the remaining solutions.

OPTSTOR has a free-format input and runs on either a VAX or IBM PC. The program's methodology, assumptions and application to a demonstration system are discussed.

BACKGROUND

To control the overloading of storm or combined sewer systems, many different strategies have been proposed. For instance, real-time microcomputer controls, disconnection of roof drains and the use of a separate pipe to convey weeping tile flows have been tried. The use of distributed in-system storage is another approach which has been implemented in certain Canadian cities such as Edmonton and Saskatoon. A computer model for the design of such storage, consisting of off-line or in-line subsurface units, is the subject of this paper.

In a complex network of interconnected sewers, it is difficult to establish the most suitable locations and volumes required to provide sufficient relief. In practice, a designer would have to proceed on a trial-and-error basis. For each storage configuration, a time-dependent, open-channel network computer model would have to be run to determine the adequacy of the proposed solution. Of course, there would be no assurance that the relief measures were in fact cost-effective.

In view of significant differences in costs for alternative storage solutions for the City of Edmonton, MacLaren developed a computer model known as OPTSTOR nearly ten years ago. In combination with the Storm Water Management Model (SWMM) RUNOFF and EXTRAN Blocks, OPTSTOR is essentially a tool for determining cost-effective locations and volumes for storage in a surcharged system requiring relief.

The original OPTSTOR program was limited or deficient in several ways:

a) only applicable to local off-line storage

b) inefficient 'search' algorithm limited the network size to fewer than 10 pipes

c) VAX minicomputer version only

d) inadequately documented

e) overly simplistic linear cost function

The objectives of the current project, begun at the start of this year, were to review these limitations/deficiencies and to implement those improvements which are feasible. All of these objectives have been fulfilled as follows:

a) applicable to all four combinations of local/trunk and off-line/in-line storage

b) utilization of the Complex Method has greatly improved speed of solution and maximum problem size

c) available on VAX and IBM PC

d) clearly documented

e) incorporation of a bilinear cost function with allowance for a startup cost

As a result of these improvements, OPTSTOR runs much more efficiently and is easier to use.

METHODOLOGY

To illustrate how formidable the problem of allocating storage is, for a network of 7 pipes in series there would be 10^7 combinations if only 10 values of volume were possible at each junction, as well as at the upstream end.

The OPTSTOR model is a simplified representation of the physical network. Key assumptions are:

- pipes arranged in series (no loops or branches)
- steady-state flow
- closed conduit flow
- head losses described by Manning's Formula

The application of this model to an actual network will be described in the sequel.

At each pipe end, except for the downstream end, there can be a storage unit. The program treats the ratios R of the stored flow to the storable flow at the pipe ends, termed nodes, as the independent variables. Due to economic considerations, the maximum value of R is limited to 0.9. Once all the ratios are given, the program calculates flows, heads, storage volumes and costs. The heads must not exceed maximum allowable values. If all constraints are satisfied, the set of R values at each node is called a (feasible) solution.

There are two major components in OPTSTOR:

- development of initial feasible solutions
- improvement of initial solutions

Development of Initial Feasible Solutions

At the outset, the existence of a solution is established by allocating maximum storage, R=0.9, at each node, where storage is permitted. If a solution exists, then the need for any storage at all is checked.

Should nonzero storage be required, the program hunts for the simple case of a solution concentrated at a single node. If there are n nodes, there can be from 0 to n such concentrated solutions. The remaining initial solutions are developed in two steps: (i) determine the minimum uniform ratio R_o at each node which yields a feasible solution, and (ii) select "random" values of R between R_o and 0.9. The term "random" is intended to imply that the solutions are sufficiently different from each other that they represent diverse points in the solution space.

The required number of initial feasible solutions ranges from 2n for n<10 to n+1 for n>16; it is 18 for n=10,11,...,16.

Improvement of Initial Solutions

The Complex Method, due to Box (1965), is used to generate improved (i.e., lower cost) feasible solutions. The set of feasible solutions is called the solution complex. By systematically modifying the most expensive solution, a new solution which is no longer the most costly is defined. The process continues iteratively until convergence is attained. More details of the procedure are provided in the following paragraphs.

The most expensive solution is reflected and stretched, by a factor of 1.3, about the centroid of the remaining complex points. Use of the over-reflection factor of 1.3 enables the complex to expand whenever possible, thereby encompassing a greater range of solutions. The objective is to produce a feasible solution which is cheaper than the original second most expensive solution.

Problems can arise if either the aforementioned centroid or the new point is infeasible or too costly. If the centroid is the problem, then a "reduced" centroid is obtained by successively omitting the most costly complex point until a sub-complex is obtained whose centroid is "good" (i.e., feasible and cheaper than the second most expensive solution). It is possible that the sub-complex could consist of only one point -- the least costly solution. On the other hand, the new point obtained by over-reflecting about the (reduced) centroid can also not be good. Should this occur, it is modified by bisecting the distance between itself and the reduced centroid. The latter process is repeated until the modified point is good or is so close to the reduced centroid that it is set equal to this point.

Convergence is assumed when the maximum absolute difference between the R values of the most and least costly solutions in the complex are within 0.001 for five consecutive iterations.

Hydraulics

The closed-conduit flows in the pipe series are modelled as being steady by means of Manning's Formula. With the convention that nodes and pipes are labelled from 1 to n, consecutively from upstream to downstream, continuity at a node j is expressed as

$$Q_j = Q_{j-1} + I_j - O_j - S_j$$

in which the various flow components are

Q_{j-1} ... upstream flow
I_j ... local inflow
O_j ... flow diversion (outflow)
S_j ... stored flow
Q_j ... downstream flow

The storable flow is based on the location of storage as shown in the following table.

Location	Storable Flow
local	Inflow (= I_j)
trunk	total flow (= $Q_{j-1} + I_j - O_j$)

In either event, the ratio R (stored flow/storable flow) cannot exceed 0.9, as explained previously.

By means of the same loss equation used in the EXTRAN Block (viz., Manning's Formula), the change in head is calculated from node to node. It is assumed that the pipes are full or surcharged. Hence, if the conservative assumption is made that the hydraulic grade line and the energy grade line are coincident, then (in Imperial units) the head loss H in a pipe is calculated as follows:

$$H = 4.665\ (n\ Q)^2\ L/D^{5.33}$$

where n is the Manning's roughness coefficient, Q is the pipe flow, D is the diameter and L is the length. Local losses can be combined with pipe losses by increasing n appropriately. Should the flow in any pipe not be full, then OPTSTOR sets the head equal to the obvert.

In a superpipe, there is zero head loss. Thus, in any pipe whose upstream end is a superpipe, the head loss is calculated on the basis of the input data for the downstream section while the upstream part has no loss.

Storage Volumes and Costs

In order to develop costs for storage, it is first necessary to relate the stored flow (i.e., reduction in peak flow) to the required storage volume. This is achieved by means of SWMM RUNOFF Block simulations. More specifically, the relations developed are of the form

$$V = kAR^m$$

where V is storage volume, k is a constant, A is impervious area, R is the ratio of stored flow to storable flow and m is a constant exponent. For the four locations/types of storage considered, the values of k and m are tabulated.

Storage Location	Storage Type	k	m
local	off-line	3320	1.59
local	in-line	2620	0.50
trunk	off-line	4600	1.62
trunk	in-line	3630	0.62

Costs for storage depend on many factors including depth, length of a superpipe and soil conditions. There could be a fixed startup cost, in addition to a cost proportional to the volume. There is a provision in OPTSTOR to express the cost as a linear function of volume V with an optional second rate. The cost is a continuous function, except possibly at V=o (startup cost).

OPTSTOR AND ITS APPLICATION

The computer program is based on the ideas and algorithms of the previous section. To encourage wide distribution of OPTSTOR, a User's Manual with complete examples of its use has been prepared. The software will run on either a VAX minicomputer or an IBM PC. OPTSTOR has a free-format input.

Preliminary testing of the program indicates that execution times on an IBM XT, with an 8087 co-processor, are about ten times as long as on a VAX 11/780.

Before using OPTSTOR, one must run the RUNOFF Block of SWMM to model system inflows from storm runoff for either historical storms or a design event. Then, the EXTRAN Block simulates the time variation of the heads and flows in the system. Should the maximum allowable heads be exceeded, each line (i.e., pipe series) is considered separately in OPTSTOR to determine cost-effective storage requirements. On account of the different approaches taken in OPTSTOR and EXTRAN, the storage solution obtained in the former should be confirmed in the latter. Indeed, several iterations of the two programs may be required before a final storage configuration is reached.

An existing trunk sewer in the Town of Vaughan near Bathurst and Centre Streets was selected to demonstrate the capabilities of OPTSTOR. This particular system was chosen for its simplicity, as a more complex network might obscure the function of OPTSTOR.

The total length of the system is some 8400 ft, with pipe diameters ranging from 4.5 to 6.9 ft. The design of the system was based on the 1:5 year rainfall in flow hydrographs derived from SWMM RUNOFF simulations of the tributary drainage area of approximately 500 acres.

According to EXTRAN simulation, the peak flow of approximately 500 cfs would be conveyed with only minor surcharges (less than 0.6 ft). To be useful as a demonstration system for OPTSTOR, it was necessary to increase artificially the peaks of some inflow hydrographs. This produced a heavily surcharged system, with unacceptably large peak heads, to which OPTSTOR could be applied more meaningfully. As expected, the case of trunk in-line storage proved to be the most expensive of the four cases, with the storage being somewhat concentrated.

Discussion

The original objectives of this research were to generalize and upgrade the OPTSTOR computer program for the cost-effective allocation of storage to a sewer system. For instance, the program now treats four types/locations of storage instead of one as in the first version of OPTSTOR:

> local off-line, local in-line, trunk off-line, trunk in-line

A User's Manual has been written and an IBM PC version has been created. The cost function has been generalized to being a bilinear function of volume. Other improvements include the introduction of free-format input, addition of more error messages and transformation to a more structured Fortran source program (important for maintenance and future updates).

Though all of the foregoing changes to OPTSTOR are useful, the most significant change was the replacement of the 'constructive' approach previously adopted by the Complex Method, together with a systematic way of generating initial solutions. As a result, the program is more efficient, yields better solutions and is applicable to larger networks.

ACKNOWLEDGEMENTS

The authors are thankful for the financial assistance provided for this research by the Ontario Ministry of the Environment. We gratefully acknowledge the assistance of Wan Wong and Mark Stirrup of the Ministry. Jim Gibson and Geof

Kearns of MacLaren Plansearch Inc. made valuable contributions to the development of OPTSTOR.

Technology Transfer Conference

Poster Presentation

Extraction & Concentration Method for Chemical & Biological Testing of Groundwater

by: J. Brady, A. Horton, K. Shaw, T. Harrison & G. Thomas

by: ONTARIO RESEARCH FOUNDATION, MISSISSAUGA, ONTARIO

INTRODUCTION

There is a need for the development and validation of test protocols to assess the degree of leachability and mobility of potentially hazardous materials contained in landfill disposal sites. A detailed chemical analysis and identification of all chemical species in leachates and groundwater is desirable, but such survey type analyses are time consuming.

Short-term biological tests are attracting interest as a basis for possible regulatory purposes. The reason is that these tests provide some predictive value regarding health effects. The overall goal of this program is to develop and validate concentration methods for organic chemicals from groundwater for use with the Ames bioassay.

SELECTION OF CHEMICALS

Initially, it was necessary to select a limited number of chemical compounds for inclusion in an aqueous solution ("cocktail mix"), in order to permit the validation of isolation/concentration techniques and measurement methods of the concentrates. The guidelines used for selecting the reference compounds were:

- to provide a wide selection of functional groups
- to represent, where possible, a range of pertinent physical properties such as volatility and polarity
- to choose, where possible, known water pollutants
- to select, when possible, halogenated derivatives of several parent componds
- resistance to degradation
- to include known mutagenic compounds

The compounds selected for inclusion in the "cocktail mix" are listed in Table I. All the chemicals listed (with exception of 2-Nitrofluorene) have appeared on lists relating to contaminants reported: viz. cancer risk assessment, chemical hazard information profiles (CHIP), and exposure assessments. The presumed mutagens on the list are indicated by means of an asterisk.

CHEMICAL TESTING

Preliminary chemical data was obtained by direct injection of suitable aliquots (1-3 µL) of the individual compounds initially, and then of a combined mixture of the compounds into a gas chromatograph/mass spectrometric (GC/MS) system. The system used was:

> HP Model 5890A series capillary GC with an HP 5970A Mass Selective Detector. The data system was an HP ChemStation with an HP 9816S computer and HP 9133XV disc drive printer.

Data was obtained for all the compounds using both total scan and selected ion monitoring procedures. Either or both methods were used for identification and quantitation during the validation of extraction-/concentration techniques for recovery of the target chemicals from groundwater. In Table I the compounds are listed together with their respective retention times and the major ions (m/e) present in their mass spectra.

CONCENTRATION METHODS

Solutions of the selected chemicals at 50 µg/L concentrations have been prepared and pumped through accumulator columns containing XAD-2.

The effects of water pH, column dimensions, flow rates through the columns and desorption methods on the collection efficiency of the adsorbent for the target compounds will be presented.

Concurrently, a large scale purging and trapping apparatus (20L) was utilized to investigate the collection of volatile target compounds. Parameters such as water volume, purge flow rates, purge times and compound collection (adsorbent or cryogenic trapping) on the recovery of target compounds will be presented.

TABLE I

ORGANIC COMPOUNDS SELECTED for "COCKTAIL MIX" to be USED in VALIDATION STUDIES for EXTRACTION/CONCENTRATION PROCEDURES for the ISOLATION OF ORGANIC COMPOUNDS from GROUNDWATER and SOLID MATRIX MATERIAL

●	Alcohols (none)	
●	Aldehydes (none)	
●	Aliphatics	* 1,2-dibromoethane 1,2-dichloropropane
●	Amines	* β-naphthylamine 3,4-dichloroaniline
●	Aromatics	o-xylene 1,2-dichlorobenzene Hexachlorobenzene 4,4-dichlorobiphenyl
●	Esters (none)	
●	Esters/Ketones	Methyl isobutyl ketone
●	Carboxylic Acids	Isobutyric acid
●	Phenols	o-cresol 2,4,6-trichlorophenol 4-nitrophenol
●	Nitrogen Compound	Quinoline * 2-nitrofluorene
●	Polycyclic Aromatic	Methyl naphthalene (α or β) Fluoranthene * Benzo[a]pyrene 9,10-dimethylanthracene
●	Sulphur Compound	Benzothiazole
●	Pesticides (none)	
●	Phthalates (none)	

* known mutagen

TABLE I

Gas Chromatographic and Mass Spectral Data for Chemicals in "Cocktail Mix"

Compound	Retention Time (min)	Base Peak in Mass Spectrum
1,2-dibromoethane	2.35	27
o-xylene	3.53	91
1,2-dichlorobenzene	5.84	146
o-cresol	6.27	108
Benzothiazole	8.99	135
Quinoline	9.20	129
2-methylnaphthalene	10.20	142
2,4,6-trichlorophenol	11.07	196
3,4-dichloroaniline	12.10	161
4-nitrophenol	13.57	139
β-naphthylamine	13.73	143
Hexachlorobenzene	15.81	284
4,4'-dichlorobiphenyl	16.72	222
Fluoranthene	19.74	202
2-nitrofluorene	20.26	165
9,10-dimethylanthracene	20.51	206
Benzo[a]pyrene	33.26	252

APPLICATION OF A FUGACITY MODEL TO MUNICIPAL WASTEWATER TREATMENT

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ABSTRACT

Many of the synthetic organic chemicals produced commercially are toxic to biota and are frequently discharged into sewer systems. This means that biological treatment plants must not only reduce BOD, suspended solids, and often nutrients, but, if possible, prevent organic chemicals from entering the aquatic environment.

To improve the removal of synthetic organic chemicals in biological wastawater treatment plants a better understandig of the fate of these chemicals during treatment is needed. It is also essential to know how the physical parameters of organic chemicals and plant operating conditions influence their behavior in a biological treatment plant. A model based on the fugacity modelling concept has been developed to predict the fate of synthetic organic chemicals in a biological wastewater treatment plant. As input, the physical properties of the chemical and relevant operating parameters of the biological treatment plant are required. The removal mechanisms of volatilization, stripping, biodegradation, and sludge wasting are considered in the development of the model model.

Results show that the most important physical properties of organic chemicals affecting their fate in a sewage treatment plant are the octanol-water partition coefficient, Henry's Law constant, and the biodegradation rate constant. The effect of different plant operating parameters, such as sludge age, aeration rate, sludge wasting technique, on the removal of organic chemicals are also evaluated. If the sludge age is reduced below 5 days, thus inhibiting the biodegradation of organic chemicals, then other processes become more significant and octanol-water partition coefficient and Henry's Law constant determine whether the organic chemical is stripped during aeration, volatilized during sedimentation or sorbed to sludge during primary and secondary treatment. However, if the sludge age is longer than 5 days, biodegradation may significantly change the fate of synthetic chemicals.

Increasing the aeration rate in the biological treatment step seems to enhance the stripping of those organic chemicals which have low octanol-water partition coefficients, high Henry's Law constants and are moderately biodegradable. The model shows however, that an increase in MLSS may reduce the amount stripped. In general, an increase in MLSS improves the removal of organic chemicals. It has also been found, that sludge wasting methods (mixed biological and primary sludge wasting or separate wasting) not only influence the overall removal efficiency of the plant for organic chemical but also determine the amount biodegraded and removed from the plant with the waste sludge.

The model proved to be effective in predicting the fate of organic chemicals and their concentrations in the plant effluent, aeration off-gases, and in waste sludges. It may be useful for improving the performance of existing plants, or to select design parameters for new plants.

KEY WORDS : fugacity model, biological wastewater treatment plant, octanol-water partition coefficient, Henry's Law constant, biodegradation rate constant, volatilization, stripping, sorbtion, mixed liquor suspended solids (MLSS).

MULTIMEDIA ENVIRONMENTAL AND HUMAN EXPOSURE ASSESSMENT OF ORGANIC CHEMICALS. Donald Mackay, Sally Paterson, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario, Canada, M5S 1A4.

A set of fugacity-based models describing (i) the environmental fate and behaviour of, (ii) human exposure to, and (iii) consequent physiological distribution of, organic chemicals has been developed.

The initial model is a novel, simplified steady state version of previous environmental models (1,2) and describes the behaviour of chemicals which are in frequent commercial use and therefore can be expected to be discharged continuously to the environment over a period of time. Examples are pesticides, PCBs, wood preservatives, and by-products of incineration and dry-cleaning operations.

The model treats four bulk phases: air, water, soil, and sediment, which consist of specified subcompartments of fluid (air and/or water), particulate (aerosols, suspended particles, and organic matter), and other phases (fish). Equilibrium partitioning of chemicals is assumed to apply within each of the four bulk phases.

Expressions for environmental emissions and advection into, reaction and advection from, and diffusive and non-diffusive transfer between these bulk phases are incorporated in a set of mass balance equations previously developed (1). Reducing the number of key environmental media to four permits a simple algebraic solution. Unlike previous models, non-diffusive transfer processes, such as wet and dry atmospheric particulate deposition, rain washout, sediment resuspension, and leaching to groundwater, are included.

The model is applied to an environment scaled to represent Southern Ontario, as well as to an evaluative environment with similar phase proportions.

It is applied to selected chemicals which are of concern to the Ministry. These include PCBs, benzene, benzo(a)pyrene, hexachlorobenzene, and mirex. The predicted concentrations are compared with reported ambient environmental data.

The model output provides information on media concentrations and amounts, as well as an overall environmental chemical persistence. Rates of transfer between, and reaction in, compartments are calculated, permitting determination of controlling processes.

The output, in the form of environmental concentrations, serves as input to a subsequent multimedia human exposure model which calculates average human chemical intake by air inhalation and food and water ingestion.

Air inhalation and water ingestion rates, as well as fish consumption rates, are combined with the appropriate media concentrations to obtain reasonable estimates of human exposure by these routes. Existing correlations which relate soil concentrations to those of vegetation, meat, and milk, are incorporated in the model to produce approximations of exposure by these routes.

The various rates of intake of air and food and water are applied to a recently developed fugacity-based pharmacokinetic model (3) to predict chemical distribution in blood and various physiological tissues such as fat, liver, skin, muscle, etc. Sites of accumulation of chemical are highlighted and rates of transport and metabolisms are quantified.

This set of similarly formulated models can be used to produce a comprehensive picture of the pathways of a contaminant from its initial release and environmental distribution, through its exposure routes to animals and humans, to its final physiological target site.

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CLAM BIOMONITORING: EFFECTS OF TEMPERATURE AND PROCEDURAL VARIATIONS ON CONTAMINANT UPTAKE WITH NOTES ON THE DISTRIBUTION OF ALTERNATE SOURCES.

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The fresh water clam Elliptio complanata has been used by the Ontrio Ministry of the Environment for the past 8 years as an in-situ, bioaccumulating agent to detect trace contminants in water. The continued use of this popular technique has made it necessary to address a number of questions regrding the future availablity of clam stocks and the environmental factors limiting it's practical application.

Our study had two primary objectives:

1) Assess alternative sources of clam stocks.

2) Determine the environmental factors effecting clam bioaccumulation.

1) Alternative clam stocks were assessed by conducting a survey of 52 locations on 24 lakes and associated water bodies in the Muskoka, Haliburton and Kawartha Lakes regions all within a 100 km. radius of Balsam Lake. Divers explored a minimum of 500 and a maximum of 2,500 square meters at sites that were selected for ease of access by boat and isolation from obvious sources of contmination from marinas and cottges. pH values ranged from 6.2 to 8.0 and alkalinity values from 3 to 5.

E. complanata was found at all but 10 of the 52 sites investigated. At ten sites densities were between 50 to 100 clams per square meter and at three sites they were greater than 100 per square meter. These densities equal or surpass those of the traditional source at Balsam Lake indicating that alternative sources of E. complanata are available to sustain future biomonioring programs.

Lampsilis and Anodonta were much less frequently sighted and in densities impractical for biomonitoring or research purposes. They also appeared to be more common in the more northern areas of our survey.

2) To investigate the environmental factors affecting clam bioaccumulation we tested variables of temperature and procedural variations in transportation of live clams, deployment and preservation of clam tissues prior to processing. These variables were tested simultaneously during a single 21 day in-situ exposure experiment conducted in the Niagara River at Niagara-on-the-Lake. The uptake of PCB's in E. complanta was used to evaluate the effect of these enviromental variables.

The transport experiments involved maintaining clams at ambient and ice temperatures in both water and moist air. Deployment experiments included suspended cages, flat cages, compact cages, support rings, and sand boxes. Tissue processing tests included holding clams at ambient and ice temperatures for 8 hrs. and 24 hrs. before shucking and freezing. All of the clams involved in these experiments were collected from Balsam Lake and transported to the Niagara River site at the same time.

Temperature experiments were conducted simultaneously with the in-situ tests. Water from the in-situ test area was continuously pumped to an adjacent building where the water temperature was adjusted to provide a range from 5 to 25 celsius at 5 degree intervals. This provided clams in the temperature experiment with a continuous supply of water from the same source as that of the in-situ clams being tested in the river.

Preliminary results of the analysis of environmental variables affecting PCB's bioaccumulation will be presented at the conference poster session.

NUISANCE BLUE-GREEN ALGAL BLOOMS IN ONTARIO: WHY THEY OCCUR

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INTRODUCTION Bloom forming species of blue-green algae (Cyanophyta) dominate the phytoplankton communities in a number of small, eutrophic lakes and impoundments in Southern Ontario. Many of these waters are important for recreational activities because of their proximity to major urban areas which have relatively few aquatic-based recreational opportunities. Unfortunately, large blue-green algal blooms have significant impacts on boating, fishing, swimming and general aesthetics.

Although we know that excessive nutrient loading leads to blue-green algal blooms, the mechanism(s) by which dominance is attained and more desirable species are excluded remains unknown. Knowledge of this mechanism should lead to improved techniques for controlling nuisance blooms, particularly for systems in which reduction of nutrient loading is impractical. This presentation describes a blue-green algal bloom and associated water chemistry in eutrophic Heart Lake, near Brampton, emphasizing the role of CO_2 in influencing phytoplankton community composition and the factors controlling CO_2 levels.

METHODS Heart Lake was sampled twice monthly during May-September, 1986. Water samples were analyzed for pH, alkalinity, total and dissolved P, total and dissolved Kjeldahl N, chlorophyll a and phytoplankton species composition. Water temperature, dissolved oxygen and Secchi depth were measured in the field. Theoretical dissolved inorganic carbon (DIC) and its component species, CO_2 and HCO_3^-, were calculated from pH, alkalinity and temperature.

RESULTS AND DISCUSSION Relationships have been reported in the literature between blue-green algal dominance and environmental factors such as temperature, anoxia, CO_2 depletion, low N/P ratios and nitrate depletion. These factors have a common link - highly reduced sediments - and their interactions are summarized in Table 1.

TABLE 1. SUMMARY OF RELEVANT EVENTS IN ANOXIC WATERS.

1. Warm temperatures in productive waters lead to depletion of O_2 and NO_3^- in surface sediments.

2. As a result of O_2 and NO_3^- depletion, redox values in surface sediments decrease and Fe^{+++} is reduced to Fe^{++}, allowing diffusion of PO_4^{---} into overlying waters. This stimulates production and lowers N/P ratios in overlying waters.

3. The rate of microbial CO_2 production decreases because O_2 and NO_3^- are in short supply. Alternative biochemical pathways for respiration are less efficient than electron transport chains supplied with O_2 or NO_3^- as terminal electron acceptors.

In Heart Lake, blue-green algal dominance was best described by changes in CO_2, rather than light, temperature, N/P ratios or HCO_3^-. High CO_2 levels above atmospheric equilibrium in early summer (approx. 15 µM), which could only have been caused by a high rate of aerobic microbial respiration exceeding degassing and photosynthetic consumption rates, coincided with low blue-green abundance. Low CO_2 levels in late summer, which coincided with high relative abundance, were probably due to a declining rate of microbial production as sediments became limited by O_2 and NO_3^-, and increased photosynthetic demand.

CONCLUSIONS

1. Low levels of CO_2 are the likely cause of blue-green algal dominance in eutrophic waters, although further laboratory and field experimentation is required.

2. CO_2 is seen as a factor which affects algal community structure but not the algal 'carrying capacity' of the system.

REMOTE SENSING DETERMINATIONS OF NORTHEASTERN ONTARIO LAKE CHARACTERISTICS

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ABSTRACT

This remote sensing project was designed to examine the feasibility of using remotely sensed data for the determination of surface water quality characteristics of lakes in Northeastern Ontario, with a special focus on discriminating between acidic (pH < 5.5) and non-acidic lakes. Further, the project involved the comparison of a selected number of sensors to undertake such tasks. During 1986-87, focus of attention was paid to establishing associations between satellite and airborne reflectance data and lake water quality parameters. Lake data sets included: for the Sudbury area, data derived from the S.E.S survey (1974-1976), the A.P.I.O.S. survey (1981-83), and a field survey north of Lake Wanapitei of 139 lakes in August of 1986; and for Algoma District in the Montreal and Batchawana rivers area, a field survey of 151 lakes, also in August of 1986.

Based on the results of this project as well as those that can be found in the literature, it is clear that several water parameters can be predicted with confidence using satellite or airborne digital data. This is particularly evident for Secchi disk depth and dissolved organic carbon. Using regression analyses, the associations (expressed by multiple correlation coefficients) between these two parameters with Landsat MSS reflectance data are of the order of 0.75 and 0.70, respectively; and 0.81 and 0.89, respectively, using Landsat TM reflectance data. Chlorophyll *a* and other water quality indicators may also be predicted, but with much more difficulty (multiple correlation coefficients of 0.63 or less). The remote sensing data also enable image processing techniques to detect gross differences between: acidic/non-acidic lakes; and, in relative terms the low/high trophic status of the lakes.

The ability to estimate lake characteristics, using multiple regression models or image analysis techniques, improves very dramatically with increases in the spatial and spectral resolution (especially the latter) of the remote sensing data.

This is seen as one moves from Landsat MSS to Landsat TM. This is also the case with airborne sensor data but the experience, up to this point in time, with these data for this project was such that "too much" remotely sensed data was available compared with field data. That is, airborne data would be an excellent water monitoring tool for small numbers of lakes for which more than one field site per lake has been examined. The latter data sets are inappropriate for synoptic surveys.

A number of problems remain as barriers to the fully operational use of remotely sensed data for water quality monitoring. Two in particular are: a) haze/cloud-covered images; and b) automization of analysis procedures. A number of approaches are being experimented with to minimize the former problem with respect to haze, but obviously totally obscuring cloud cover is impossible to overcome. The latter problem is less difficult to solve but may be time-consuming. Another difficulty that is recognized here but was not encountered often in the present project is the discrimination of acidic lakes that are coloured, i.e. the "brown water", acidified lakes.

Work that is presently underway using multivariate statistical analyses and image analysis techniques is aimed at refinement for the purposes of increasing the precision of the lake parameter predictions and the discriminations between various levels of trophic status, as well as between acidified and non-acidified lakes. Coarse-resolution (spatial and spectral) Landsat MSS data provide little opportunity for temporal lake analyses. On the other hand, temporal monitoring of lake water quality for large-area studies is a definite possibility because of the superior data currently being recorded by Landsat TM and the even better data that are promised by future sensors. More precise, small-area studies should not employ current satellite data, but instead should rely on advanced airborne sensors, especially if thermal data can be provided in addition to bands in the lower portion of the electromagnetic (visible) spectrum.

The observations reported here linking remotely sensed data with lake water quality parameters or lake classes emphasize the relationships that associate spectral reflectance measurements with lake transparency and related variables. For the generally dilute, low productivity lakes of the Sudbury study area, transparency in the form of Secchi disk depth is primarily controlled by DOC rather than the phytoplankton population as expressed by chlorophyll concentrations. These points are of fundamental significance in Northeastern Ontario, and in other areas with similar lake systems. Elsewhere (even to some extent in the Algoma study area), with lake systems that are not similar, different approaches to establishing relationships between lake water quality characteristics and remotely sensed data may be required.

While these analyses are preliminary in the sense that less than a year's work has been involved, I am confident that remote sensing will soon take a more prominent role in lake water quality monitoring programs. In terms of monitoring lake acidification or trophic status, it is recognized that regression models provide estimates of individual lake parameters that may be indicators of acidification/trophic level, not conclusive evidence. But then that is also the case with these parameters when derived from field programs. The advantage that remote sensing brings to such surveys is the fact that many more lakes over broad geographical regions can be examined compared with more costly field work, although the latter will never be entirely eliminated. If the results described here are applicable for other images/locations with similar lake systems, remote sensing will most definitely assist in the assessment of the spatial extent of lake water quality characteristics in Ontario.

ROBUST TREND ASSESSMENT OF WATER QUALITY DATA SERIES

Byron Bodo[1], Keith W. Hipel[2], and A. Ian Mcleod[3]

Trend analysis of water quality data series obtained from ambient river monitoring programs like Ontario's Provincial Water Quality Monitoring Network (PWQMN) is required: 1. to alert authorities to water quality degradation; so that, appropriate corrective action may be initiated; 2. to evaluate the performance of pollution abatement measures usually undertaken at great public and private expense. Standard parametric statistical procedures are inappropriate for water quality data series typically exhibiting such confounding features as uneven spacing in time, high background variability (low signal-to-noise ratio), nonnormality (skew), numerous outliers, autocorrelation, seasonal periodicity, etc.. While variants of the nonparametric Mann-Kendall test [1] have proven robust against most of these factors [2,3,4,5,6,7,8], a serious problem remains in that almost all rigorous trend tests rest on the assumption of monotonic trend, or very generally, trends which always proceed in the same direction, either increasing or decreasing. Experience with PWQMN records has shown that nonmonotonic trends may indeed occur; consequently, blind reliance on abstract test statistics may yield inaccurate conclusions. Thus the object of the present research was to develop robust graphical procedures for qualitative visual trend analysis as corroborative evidence for formal trend tests.

To appreciate the concept of trend, consider the elementary additive time series model for some variable X at time t,

$$X_t = T_t + S_t + \epsilon_t \qquad (1)$$

where T_t is trend, S_t is the seasonal component and ϵ_t is a residual noise term. Trend T_t merely represents change over time in the "mean" level of process X_t and hence, is a somewhat arbitrary concept defined according to the time scale of measurements and the time horizon of interest. Assume T_t represents gradual trend. Term S_t represents regular annual periodicity that is assumed not to evolve with time. This elementary model is generally applicable to the analysis of the majority of water quality data series generated by long term ambient river quality monitoring programs such as the PWQMN for trend detection over horizons of 5 years or more.

The object of simple time series analysis is to decompose data series X_t into deterministic trend and seasonal components and the irregular term ϵ_t. If T_t (S_t) is weak and may be ignored, S_t (T_t) may be directly determined; however, when both strong trend and seasonality are present a "catch-22" situation arises, as in principle, S_t must be known before T_t may be determined and vice versa. The impasse can be resolved by the iterative approach of Mcleod et al. [9] which employs a first approximation of T_t (S_t) to generate a first approximation of S_t (T_t) that is used to refine the initial estimate T_t (S_t), etc..

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Smooth, nonmonotonic, nonlinear trend T_t is traced through unevenly spaced, noisy data series by the powerful robust locally weighted regression (RLWR) procedure invented by Cleveland [10,11]. Generally, RLWRm is an iterative sequence of local least squares regression at each data point X_i with its m nearest neighbours, weighted by distance from X_i, followed by the global assignment of robustness weights according to the distance from X_i to the locally weighted regression estimate to minimize the influence of outliers. Low powered RLWR, e.g. RLWR12, trend lines reveal seasonal periodicities, abrupt jumps and other temporally local phenomena. High powered RLWR75, RLWR150, etc., yield smooth lines characterizing medium and longer term trends. A robust seasonal function S_t is defined as the moving seasonal median (MSM) of the historical series aggregated by date within the year. Employing RLWR and MSM together in the context of model (1) yields for unevenly spaced series a robust analogue of conventional time series analysis, e.g. [12]. Attention could focus specifically on trend T_t or seasonality S_t, or these may be recomposed into useful forms such as seasonally adjusted trend, i.e. trend free of seasonal distortions, and trend adjusted seasonality, i.e. long term seasonal norms projected onto current robust mean levels when significant trend has been observed.

Figures 1 and 2 illustrate the application of the method to a dissolved oxygen (DO) series. Figure 1 presents the direct application of RLWR to the raw data series. The RLWR12 trend line clearly shows the strong seasonality present. The RLWR75 trend line, after a rise from 1977 to 1982 shows a distressing drop of 2.1 mg/L to mid 1986 suggesting that critical DO conditions are impending. Accounting for seasonal effects, Figure 2 shows correctly that only a 1+ mg/L drop, connected with above normal temperatures, occurred over 1982-83 since which levels have increased slightly. The RLWR75 line of Figure 1 was distorted by strong seasonality compounded by failure to obtain winter samples in 1986, effects that would likewise corrupt formal trend tests not robust against seasonality.

Reliable trend assessment of typically ill-behaved water quality data series will require both graphical analysis and rigorous statistical testing. The examples illustrate the power of well designed graphical displays to communicate complex quantitative information. Indeed, the significance of graphical methods is increasingly being recognized [11,13,14]; although, we caution that graphics can be as readily abused as more formal statistical methods. The techniques outlined herein have been effectively demonstrated in the analysis of physical and chemical data series at 6 PWQMN sites in the Don River basin. Procedural details and results will be reported in forthcoming reports.

Fig. 1. DO TRENDS

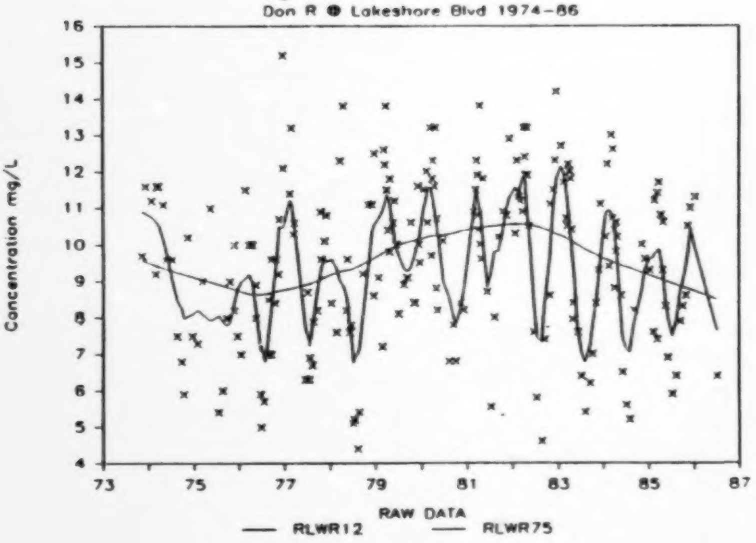
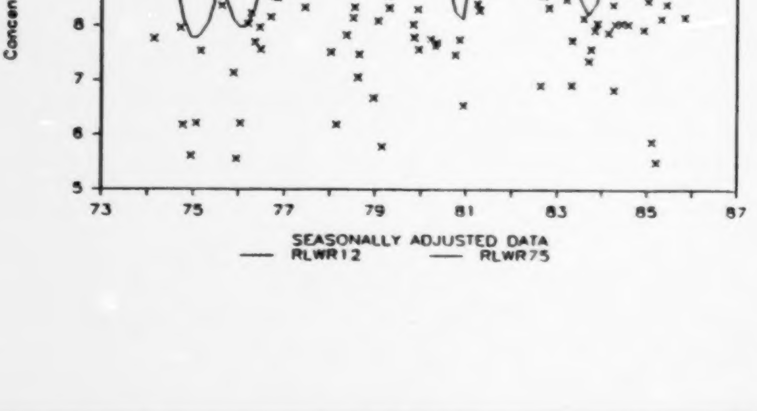


Fig. 2. DO TRENDS



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REPRODUCTIVE OUTCOMES IN SOUTHWESTERN ONTARIO

1980 TO 1985

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The aim of this study is to determine if the consumption of drinking water from the St. Clair River was associated with abnormal outcomes of pregnancy and adverse first-year-of-life outcomes in residents of Kent and Lambton Counties in the six year period, 1980 through 1985.

The investigation has four phases, the first of which has been completed. Comparisons of the six year total incidence rates of congenital anomaly, low birth weight, and neonatal, perinatal and infant death in the two counties with those of the ten county Ontario Southwest Region and with provincial rates revealed no statistically significant differences. The incidence rates of spontaneous abortion in Kent County as a whole, and in the potentially exposed and nonexposed subgroups were significantly high, with relative risks ranging from 1.44 to 1.71. Conversely, Lambton County had a significantly low incidence rate of spontaneous abortion (RR = 0.55; 95% C.L. - 0.49 - 0.62). The "exposed" subgroup in Kent County had a significantly low rate of stillbirth (RR = 0.40; 95% C.L. = 0.17 - 0.96); whereas the rate of Kent County as a whole was virtually identical to those of the comparison groups. The results of this phase of study did not support an association between drinking water from the St. Clair River and the outcomes of interest for the following reasons:

1) The rate of spontaneous abortion in the "exposed" subgroup in Kent County was lower than those of the "nonexposed" subgroup and the county as a whole.

2) The rate of spontaneous abortion in Lambton County was significantly low.

3) The rate of stillbirth in the "exposed" subgroup in Kent County was also significantly low.

4) The rates of the remaining outcomes did not differ from expectation.

The second phase of the study consists of detailed interviews of the 490 women who experienced 508 pregnancies resulting in 666 abnormal outcomes in the period of study and of a matched control group of women who had normal children, to determine their exposures to St. Clair River water and to other factors which might have influenced exposure and/or outcome during the index pregnancies. The matching variables chosen were: county of residence at the time of the birth (Kent or Lambton), date of birth (± 60 days), maternal age (± 1 year), parity (± 1), and sex of the child. We have, so far, selected matched control mothers for 402 (79%) of the 508 case pregnancies. We expect to obtain a further 101 controls leaving only five cases unmatched (1%). As of 31 July, 1987 we were unable to locate or had been refused permission to contact, 42 (9%) of the 490 mothers of cases. Of the remaining 448, we have contacted 261, 237 (91%) of whom agreed to be interviewed. We have also contacted 270 eligible control women. The interview schedule has been pretested and modified slightly to clarify and simplify some of the questions. Tracing and contacting of eligible respondents is continuing while interviewing is in progress.

In the retrospective cohort phase of the study we are comparing the outcomes of pregnancies in women who were exposed to drinking water from the St. Clair River at the time of five specific chemical spills with those of the following three, presumably nonexposed cohorts:

1) Women whose pregnancies occurred at the same time as the spills but who resided in areas of Kent and Lambton Counties where they were likely not exposed to St. Clair River water;

2) Women resident in the same areas as the exposed cohort but whose pregnancies occurred at times other than the spills; and

3) Women resident in Elgin, Huron and Middlesex Counties whose pregnancies occurred at the same time as the spills.

We estimate that 1,150 pregnancies occurred in the "exposed" cohort, 3,100 in the first cohort above and 1,300 in the second. A sample of the former group will be selected to match the women of the exposed cohort on age and parity. Confirmation of exposure status and other important details regarding the index pregnancies will be sought from the participants in brief telephone interviews.

The fourth phase of the study consists of a comparison of the outcomes of all pregnancies that occurred among Native women of the Walpole Island Reserve with those of women of the Sarnia Reserve. This comprises a direct comparison between a heavily exposed and a virtually nonexposed population since the former group consumes fish and wild game from the St. Clair River as well as using it as a source of drinking water; whereas the Sarnia Band receives drinking water from the City of Sarnia and consumes no more fish and game from the river than does the non-Native population of Lambton County. In the seven year period, 1980 through 1986, 380 livebirths occurred in the Walpole Island Band and 117 in the Sarnia Band. From this, we estimate that 540 and 170 pregnancies occurred in each group. All women who experienced pregnancies will be interviewed by Native interviewers to determine:

1) Their exposures to the St. Clair River from drinking water, fish and game consumption;

2) Other exposures during the index pregnancy; and

3) The outcomes of the pregnancies.

We estimate that data collection and analysis for the final three phases of this project can be completed by February, 1988 and a draft report submitted to the Ministries of Health and Environment by the end of March, 1988.

ABSTRACT

Regional Analysis of Low Flow Characteristics

When undertaking environmental investigations related to watercourses, the knowledge of hydrologic conditions which exist during low flow conditions can be of primary importance. The identification of suitable low flow characteristics within a watercourse is most easily accomplished using continous hydrometric data recorded for the stream. However, this is limited to the availability of suitable long term discharge records at the location of interest. The objective of this investigation is to develop a practically oriented technique for estimating low flow characteristics at ungauged locations in the Province.

Initially, a background review was undertaken to confirm the most appropriate single station and regionalization techniques. It was confirmed that the Gumbel III extreme value distribution generally has been found as the best fitting distribution for low flow data of various durations for analysis of single station records. However, other investigations concluded that the Gumble III distribution becomes unstable if the sample has a skewness of less than -1.08 and it has been concluded (eg Condie and Cheng) that while the Gumbel III Distribution should be adopted as the basic method for low flow frequency analysis that, as an alternative distribution for samples with large negative skewness the Three Parameter Log Normal Distribution should be used.

The background review also confirmed that several investigations utilized statistical multiple linear regression techniques to regionalize low flow characteristics. It was found that low flow characteristics depend largely on a number of physiographic and meteorologic indices. On the basis of the literation review, it was decided to include the following parameters in the development of a physiographic data base for the Southwestern and West Central Regions of Southern Ontario: drainage area, (DA), mean annual snowfall (MAS), mean annual precipitation (MAP), mean annual runoff (MAR), area controlled by lakes and swamps (ACLS), Latitude (LAT), Longitude (LONG), Equivalent slope (EQSLP), 10/85 slope (OSLP), stream length (LEN), years of daily data (DYRS), and Base Flow Index (BFI).

.../2

The dependent parameters (eg. The 7 day 20 year low flow and flow duration characteristics) have been determined for 89 stations. Initially, a preliminary screening and "regionalization" was undertaken graphically by interfacing the output of the statistical analysis program with a Calcomp plotter. The graphical "regionalization" will be used as a basis for comparison to establish the degree of improvement by the statistical (regression) procedures.

The method developed will then be applied and evaluated in a test area to confirm the usefulness in predicting low flow characteristics for ungauged watersheds.

To date, the following analyses have been completed:

- extreme value analysis for 89 stations
- flow duration analysis for 89 stations
- data base of 12 parameters for 89 stations
- preliminary mapping/screening of statistical analyses and data

Work is proceeding on refining and testing the statistical regionalization technique. Ultimately, the results of the analyses will be summarized according to regional characteristics and in map format. The latter is an attempt to update the map series entitled "Low Flow Characteristics," previously published by the Ministry of the Environment.

ASSESSMENT OF ALTERNATIVE WATER TREATMENT PROCESSES ON NORTHERN ONTARIO WATER by D.R. Fisher, P.Eng. and S.J. Wyse, Ph.D.

This study, supported entirely by the Ontario Ministry of the Environment, was designed to assess the best water treatment process and treatment chemicals for the Gull Lake water supply to the Town of Kirkland Lake and adjacent communities.

Several studies have been carried out on this water over the last twenty five years. In 1963 work by C.F. Schenk of the Ontario Water Resources Commission investigated the problem of a fish like taste and odour in Gull Lake water and concluded that it was due to algae formation. The combination of a shallow lake which warms quickly and sufficient phosphorus and nitrogen gives optimum conditions for algal growth.

However, the main object of this study was to develop a treatment system which could respond to the colour and turbidity increases which occur during spring and fall.

At present the treatment of Gull Lake water is limited to chlorination and fluoridation which has little effect on any of the problems experienced with this water.

A study carried out by Proctor & Redfern in 1985 on direct filtration concluded that it was difficult to obtain filter runs of more than 10 hours without termination of the run due to turbidity breakthrough or high headloss. It was determined that the main difficulty was due to the alkalinity level which is higher than most northern waters.

After these studies proved unsuccessful it was decided to assess three alternative full treatment technologies. Firstly, a plate flocculator/plate separator technique followed by a dual media filter was employed. The method is used with considerable success on waters in Europe and had not previously been utilized for drinking water treatment in Ontario. The second technology employed a high rate upflow clarifier followed by a multi media downflow filter which has seen limited use in Ontario and has not been directly compared to more conventional forms of water treatment. The final technology used a mechanical flocculator/plate separator, which served as a more conventional pre-treatment system, followed by dual media filtration.

These pilot plant tests were carried out between January and March, a period during which the Kirkland Lake community has its highest water usage, it is also the time of the coldest water temperature. All three technologies were required to treat water from Gull Lake ranging in temperature from 0 to 2°C, a range well below that required for optimum coagulation by many chemicals.

Various coagulants and coagulant aids (organic and inorganic) were assessed on each of the process systems in order to optimize chemical effectiveness operating conditions. Filtration rates were also varied.

The following system parameters were monitored throughout the pilot testing program:

- turbidity (raw, pre-filtration, filtered)
- colour (raw, pre-filtration, filtered)
- alkalinity
- hardness
- pH
- aluminum residual
- headloss
- length of filter run

By using the results of these parameters and others it was possible to assess the relative efficiency of each water treatment system and to compare one system with the other two.

The overall assessment and evaluation of the alternative systems used in the studies show that for coloured waters with light fragile floc, the plate flocculator/plate separator method is preferred to the mechanical flocculation plate separation system. It was apparent that the lower shear force on the floc particles assocated with the plate flocculator was an advantage.

Good performance was also obtained with the upflow clarifier. However, the rise rate was very high in the clarifier and the retention time very low. Consequently, good results could only be obtained with a combination of polymers, some of which may cause problems.

Clarifier effluent quality was similar in the plate separator and upflow clarifier. However, the mixed media used with the upflow clarifier tended to give longer filter runs. Media optimization work should improve the filter runs with the dual media. The smaller area of the filter columns used with the plate system compared with the larger area of the mixed media filter used with the upflow clarifier could also contribute to the difference in filter run times. With a full scale plant 24 hour filter runs should also be obtainable with the plate flocculator and separator system.

SLOW SAND FILTRATION FOR DRINKING WATER PRODUCTION IN SMALL NORTHERN COMMUNITIES

This study, supported by the Ontario Ministry of the Environment, is designed to evaluate the production of drinking water in small northern communities by simple water treatment schemes. The purpose of this study is to develop a system incorporating slow sand filtration to suit the specific needs of each community.

Small, remote northern communities have special conditions of climate, population, and technical expertise. Specifically, water treatment systems for remote communities should have the following important characteristics:

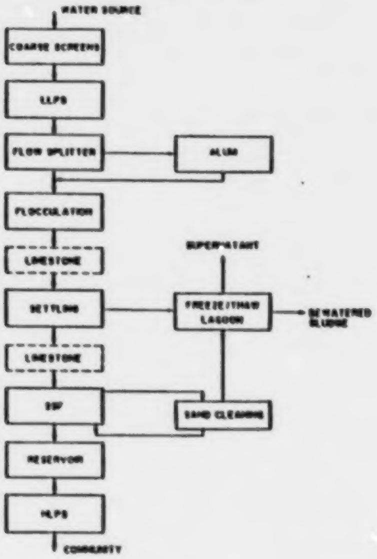
- Low capital and operating costs
- Simple to understand
- Minimum mechanical/electrical parts
- Low sensitivity to misuse
- Low maintenance and operating time
- Few chemical feed systems

Surface waters in the north are typically coloured and low in dissolved mineral content. Consequently, the main water treatment process objectives are usually to provide adequate disinfection, to remove colour, and to control the aggressiveness of the water.

Investigative work has recently been completed on slow sand filtration; however, much of this work consists of surveys of existing facilities, and the conclusions support the need for a more versatile approach. This study will investigate the design, operation, and maintenance of slow sand filters to obtain a cost-effective treatment process to suit the specific needs of each community. Since most Northern Ontario waters are coloured, simple methods of colour removal which can be associted with slow sand filtration have been studied. In addition, it may also be advisable to reduce the aggressiveness of the water by increasing the pH, hardness, and alkalinity of the water. This can be accomplished by adding limestone in the treatment process.

A possible treatment scheme incorporating slow sand filtration and colour removal is outlined in the simple process flow diagram below.

PROCESS FLOW DIAGRAM
POSSIBLE SLOW SAND FILTER PLANT


WATER SOURCE
COARSE SCREENS
LLPS
FLOW SPLITTER
ALUM
FLOCCULATION
LIMESTONE
SUPERNATANT
SETTLING
FREEZE/THAW LAGOON
DEWATERED SLUDGE
LIMESTONE
SSF
SAND CLEANING
RESERVOIR
HLPS
COMMUNITY

An alum saturator could be used as the alum feed system. A rock alum storage vessel would act as a solution saturator. A small portion of the flow would enter the vessel to produce a concentrated alum solution, which would then be returned to the main flow. An important component in the removal of colour is a regime of controlled mixing for a specific time. The mixing can be induced hydraulically, such as by spiral-flow flocculators.

As discussed earlier, the addition of limestone may be beneficial to the overall system. The process flow diagram shows two possible locations for a flow-through tank containing limestone. It seems that the location between the settling tanks and filters would be best so as not to have alum floc accumulate in the limestone bed.

For Northern Ontario coloured waters, the majority of the precipitated colour solids must be removed by sedimentation prior to slow sand filtration (SSF). SSF is not able to endure heavy solids loadings and be effective; consequently, SSF has normally had associated settling basins to ensure that much of the solid material is removed prior to filtration.

The initial stages of this study have been completed. The next two phases will involve continued laboratory testing, assembling of available literature, and further site visits to SSF plants. A critical pilot plant investigation will follow to evaluate design, operation, and maintenance conditions. Capital and operating costs will also be evaluated. A "Guidelines Manual for Design and Operation of Slow Sand Filters" will be the final result.

BP12

LOCATING AREAS OF GROUNDWATER FLOW TO SURFACE WATER. David R. Lee*, AECL, Chalk River, Ontario; Wayne C. Wager*, Ontario Ministry of the Environment, Sarnia; Peter B. Kauss, Ontario Ministry of the Environment, Toronto.

Landfill sites, both active and abandoned, mine-tailing areas and major industrial complexes have frequently been located adjacent to surface waters primarily because of transportation and process water needs of industry. While leachate plumes and attenuation zones of inland disposal sites have frequently been assessed, methods for assessing subsurface discharges directly to surface waters are largely lacking.

In summer of 1986, work was initiated in the Upper Great Lakes Connecting Channels (St. Clair and St. Marys Rivers) using a rugged sediment probe to target areas of river sediment where temperature and conductivity differed from background suggesting groundwater discharge. In this method the probe was towed along the bottom behind a slowly moving boat.

Follow-up work conducted in the St. Marys River during the summer of 1987, supports the efficiency of the method to target leachate flow areas from river sediments into surface waters.

AN EXAMINATION OF CHRONIC TOXICITY OF THIOCYANATE TO FRESHWATER FISH FOR THE DEVELOPMENT OF A WATER QUALITY CRITERION

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Cyanide is used by the mining industry for the concentration and extraction of gold and silver ores. Thiocyanate ion (SCN^-) is the major by-product of the treatment of cyanide-bearing effluent, and as such routinely appears in receiving waters. Acute toxicity testing has shown the SCN^- is substantially less toxic that hydrogen cyanide, but virtually no information exists on the sublethal effects of SCN^-. There is currently no Ontario water quality objective for SCN^-, despite the documentation of sublethal effects of SCN^- on thyroid metabolism in mammals and fish.

The aim of this research is to obtain sufficient data on the chronic toxicity of waterborne SCN^- to establish a water quality criterion. This will be accomplished by exposing various test species of fish to different levels of waterborne SCN^- and monitoring their responses based upon survival, growth, biochemical and histological parameters. Finally, we propose to apply some of the laboratory-derived biochemical and histological indicators of SCN^- toxicity to the assessment of SCN^- impact on feral fish populations in the White River drainage basin in northern Ontario.

The first year of the study will entail the exposure of various life stages of rainbow trout to different levels of SCN^- while monitoring their response through survival, growth and physiological parameters.

Previous work by Heming et al. (1985) suggested the presence of a phenomenon referred to as Sudden Death Syndrome (SDS). When fish exhibiting no obvious effects of SCN^- exposure are subjected to a stressor, there occurs an immediate (within 10 s) response characteristic of acute SCN^- (as well as cyanide) toxicity. Response signs include flared gills, erratic swimming, convulsions, spasms, pigmentation changes and death. The SDS response has been found in experiments in our lab. Preliminary bioassay results with juvenile rainbow trout (2.5 g) indicate that the 96 h LC50 values for 'unstressed' and 'stressed' fish are 65 and 45 mg l^{-1} respectively. The 'unstressed' LC50 value is calculated from the response of fish which were not stressed during the 96 h bioassay. The 'stressed' LC50 is based upon mortalities occurring after the completion of the 96 h bioassay when fish were subjected to 15 s of chasing with a hand-held dipnet.

Based upon the results of the preliminary bioassay, SCN^- exposure concentrations were selected for a preliminary four week toxicant exposure/growth trial. Juvenile rainbow trout (2.0 g) were reared at SCN^- concentrations of 0, 0.5, 5, 10 and 20 mg l^{-1} at 15°C. Trout were fed on a practical diet with each replicate having a matched, pair-fed control. No differences were found in growth, feed consumption or feed conversion efficiency between fish exposed to different levels of SCN^- or between replicates and their pair-fed controls. No significant mortalities occurred, even after the fish were subjected to the stress of netting and weighing.

From the results of the four week study, SCN^- exposure concentrations of 10, 20, 30 and 40 mg l^{-1} were selected for a 16 week toxicant exposure/feeding trial. Each replicate will be matched with a pair-fed control group. Growth and feed conversion efficiency will be monitored bi-weekly for the duration of the study. Plasma cyanide and SCN^-, plasma thyroid hormone levels, liver glycogen and liver protein levels will be monitored. Tissues selected for histopathological examination include liver, kidney, gill, thyroid and gonads.

In addition to the chronic growth examinations, our study will include an examination of the effects of pulse exposure of rainbow trout eggs and fry to SCN^-. Rainbow trout eggs will be exposed to a three hour pulse-dose of either KSCN or NaSCN, post-fertilization, and either during or after the process of water hardening. Fertilization rates, mortalities, developmental anomalies and yolk conversion efficiency will be monitored.

Based on the results of studies conducted during the first year, we will obtain a hypothetical maximum acceptable SCN^- concentration for normal egg development and growth in rainbow trout. We also hope to develop biochemical parameters, such as plasma thyroid hormone levels and histological examination, which will prove useful in the assessment of SCN^- impact on feral fish populations.

During the second year of the study, we will determine the effects of various concentrations of SCN^-, on the reproductive capacity of fathead minnows over 1+ life-cycles. The results of this study will be analyzed to determine a no effect level of SCN^- for reproduction in the fathead minnow.

In the third year of the study, we will assess the health of white sucker populations in several lakes of the White River system of northern Ontario. This system receives SCN^- effluent associated with gold metal mining operations in the Hemlo district. Assessment of the fish populations will be made in terms of age-size relationships, reproductive capacity, histopathology and biochemical indicators. The results will provide insight into the impacts of SCN^- on feral populations and will develop tools for measuring *in situ* impact.

BIOMONITORING PROTOCOLS FOR ADULT AQUATIC INSECTS: COLLECTION PROCEDURES, SEASONAL VARIATION AND DISPERSAL

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Benthic aquatic insects living in contaminated sediments can carry high organochlorine burdens. But their value as biomonitors can be limited by difficulties of sampling and of collecting enough biomass for analysis by gas chromatography (GC) (typically 5 g fresh wt.). Collection of the nocturnal, photophilic, winged adult stages is potentially simpler and less expensive. Our objectives were to: a) develop traps to collect sufficient adults to permit GC analysis for organochlorine contaminants (PCBs, HCB, OCS, QCB); b) determine minimum sample biomass that provides reasonable limits of detection; c) assess seasonal insect availability and variations in contaminant burden; and d) evaluate dispersal abilities to estimate size of area to which a sample collection pertains. We used 12V/DC battery-powered Pennsylvania-type ultraviolet light traps. CO_2 subliming from dry ice in the trap base (1 kg h^{-1}) quickly killed trapped animals. Although Trichoptera (Hydropsychidae, Leptoceridae) actively entered traps, Ephemeroptera (*Hexagenia*, *Caenis*) alighted nearby and required hand-collection. Weekly samples were taken during 2 h following sunset at Detroit R. and St. Clair R. sites beginning in early May. Adequate biomass was collected in single traps on 26 May. Thereafter, animals were abundant at sunset temperature >20° C. and wind speed <10 km h^{-1}. Mean (±1 S.E.) June Trichoptera catch was 86.5 ± 44.9 g/2 h/trap (N=6). *Hexagenia* biomass varied greatly among sites and dates (range 20 - 605 g/2 h/trap, where present). Mid-June samples at uncontaminated sites provided Hydropsychidae (Fenelon Falls, 285 g) and *Hexagenia* (Balsam Lake, 70g) for detection limit studies. Traps up to 5 km inland were monitored on calm, warm evenings to estimate dispersal distance according to a random transport model. Median dispersal distances estimated for *Hexagenia* at L. St. Clair and in the Detroit R. ranged from 2.7-6.0 km. Estimates for Detroit R. *Macronema* caddisflies were more variable (2.2-6.9 km). Other caddisflies and mayflies displayed much less dispersal.

INTRODUCTION

Results of recent studies indicate that benthic invertebrates have the capacity to accumulate organochlorine contaminants. Freshwater mussels (Kauss and Hamdy 1985), oligochaete worms (Oliver 1984) and Chironomidae (Diptera) (Larsson 1984) have all been shown to carry high contaminant burdens. This suggests the potential of these animals for use as biomonitors, since the contaminant concentrations in benthic invertebrates tends to correspond to that of the surrounding sediments (Pugsley et al. 1985).

The major difficulty in using the above organisms for such a purpose arises from difficulties associated with sampling and processing prior to analysis. Collection of adequate biomass for gas chromatography (GC), typically 5 g fresh weight, is often difficult since the animals may occur sporadically, or be closely associated with the surrounding sediments. Diver-assisted collection is often hindered by strong currents, poor visibility and heavy boat traffic in addition to requiring trained personnel and specialized equipment. Furthermore, samples collected with the surrounding sediments need extensive sorting prior to GC analysis, which may result in degradation and/or further contamination of the collected organisms.

Trichoptera (caddisflies) and Ephemeroptera (mayflies) spend most of their lives as benthic larvae in contact with the sediments. The winged adults emerge in large numbers during the summer, having one or possibly two periods of peak emergence. The adults are nocturnally active, and exhibit strong attraction to lights. Ciborowski and Corkum (In press) analysed adult mayflies and caddisflies collected from sites along the Detroit and St. Clair rivers for organochlorine contaminants and reported siginificant concentrations of contaminants. The geographical contaminant distribution pattern was similar to that found by other workers using freshwater mussels.

Collection of adult Ephemeroptera and Trichoptera for GC analysis requires little specialized equipment, can be done by minimally trained personnel, and is less time-consuming than sampling for larvae. Adults can be collected using long wave ultraviolet light traps. Since samples are not collected with the surrounding sediments, sorting time is greatly reduced. Thus, aerial adult stages of aquatic insects may be more cost efficient biomonitoring organisms than their immature benthic counterparts.

Since adult aquatic insects are capable of dispersal, there is potential for contaminant transfer to terrestrial or possibly other aquatic habitats. When completed, our study may provide some information concerning such possible contaminant transfer.

The objectives of the present study were as follows:

a) development of light traps for the collection of adequate biomass of aquatic insects for organochlorine contaminant analysis by GC.

b) determination of minimum sample size, necessary to yield reasonable detection limits of contaminants during gas chromatography.

c) evaluation of seasonal insect availability and variation in contaminant burden.

d) measurement of dispersal distance for the insects collected to determine the area over which our data are applicable.

METHODS

Light Trap Design

The light trap employed was a modified Pennsylvania type trap (Frost 1957). The trap (Fig. 1) consisted of a galvanized iron bucket having a top diameter of 30 cm, with a 12 cm wide cylindrical hardware cloth reservoir placed in the centre. Dry ice, which cooled and anesthesized the trapped insects was packed around the reservoir. Since the trap was developed with the analysis of the trapped insects for contaminants in mind, it was preferable not to allow the dry ice, which may be contaminated, to come into contact with the collected sample. The reservoir served this purpose. Dry ice sublimed at the approximate rate of 1 kg h^{-1}.

The mouth of the bucket was covered by a large funnel that emptied into the reservoir. The funnel was snapped into the bucket and secured by three flanges. A set of three 45 cm tall, 15 cm wide clear styrene vanes was mounted upon the top of the funnel. The vanes were attached to a circular aluminum top plate. A 3 cm diameter hole permitted placement and removal of a 45cm long 12V/15 watt DC fluorescent long wave ultraviolet lamp at the axis of the vanes. The light was powered by two 6V lantern batteries connected in series, or by an automobile battery.

Traps were cleaned with soap and water before use, and those parts which came into contact with the insects were hexane-rinsed. Flying insects were attracted by the light and flew towards the trap where they collided with the vanes, fell down, and were guided into the wire mesh reservoir by the funnel. On humid days condensation on the trap caused some insects to stick to the vanes or the funnel. These were shaken or picked off and added to the sample at the end of the two hours of trap operation.

Sample Collection

Adult aquatic insects were collected weekly from 19 May to 22 September 1987 at four Canadian sites along the Detroit and St Clair rivers (Table 1). The sampling season extended from 19 May to 22 September for the Detroit River sites and from 11 June to 31 August for the St Clair River sites. Samples were also collected (18-19

Table 1. Locations of sample stations.

Stn	River	Designation	Latitude (North)	Longitude (West)
1	Detroit	East Windsor	42°20'27"	82°56'56"
2	Detroit	River Canard	42°11'48"	83°06'13"
3	St Clair	Sarnia	42°54'12"	82°27'29"
4	St Clair	Sombra	42°42'02"	82°29'03"

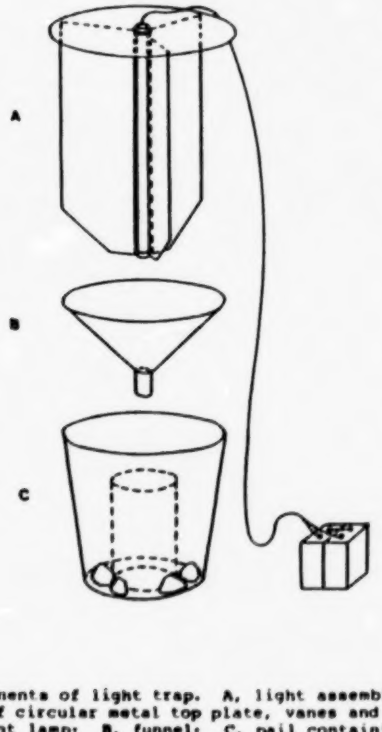

Figure 1. Components of light trap. A, light assembly consisting of circular metal top plate, vanes and 12VDC/15W UV flourescent lamp; B, funnel; C, pail containing metal window screen cylinder and dry ice.

June 1987 and 6-7 August 1987) near Balsam Lake in central Ontario and (17 August 1987) from the Ausable River near Arkona in southwestern Ontario. Samples collected near Balsam Lake and Arkona were assumed to be uncontaminated and were stored at -70°C for use in detection limit studies. Collections prior to 26 May were made by the method of Ciborowski and Corkum (In press).

Light traps were placed on a white sheet, approximately 2-5 m from the riverbank so as to provide clear exposure to the the river. Traps were operated for two h following sunset, since nocturnally active aquatic insects exhibit greatest flight activity during this period. The sheet served as a light reflector and a substrate for those insects that failed to enter the trap.

Mayflies (Ephemeroptera) tended to alight on the sheet rather than to enter the trap. They were grasped by the wings and placed into a separate sample jar or were manually added to the trap reservoir.

At the end of the two-h sampling period the light was turned off and the contents of the reservoir were emptied into one or more precleaned 500 ml amber glass specimen jars. The sheet was quickly folded to retain any insects that had landed on it. Both the specimen jar and the folded sheet were kept in a cooler containing dry ice during transport to the laboratory. On several nights the reservoirs had to be emptied hourly due to the abundance of insects.

Studies evaluating the catch of unattended traps have been deferred until 1988, pending development of a DC-powered timer switch.

Sample Processing

Samples were grossly identified as Trichoptera, _Hexagenia_ (Ephemeroptera), other Ephemeroptera, and Other Taxa (mostly Diptera and Coleoptera). The total sample was weighed as well as the sorted groups of insects. Samples were sorted at room temperature and stored at -20°C. The large size and heterogeneity of some samples necessitated subsampling. One hundred caddisflies in each sample were identified to genus and were preserved in 70% ethanol. Sorting time ranged from 30 min for small samples (< 10 g fresh weight) to 3 h for large samples (> 80 g). Sorting time increased with increasing diversity.

Dispersal Distance Studies

Studies were conducted to determine the geographical area represented by animals in sample collections. Aquatic insects were collected along Rochester Township Concession Road 4 on the south shore of Lake St Clair, and along Essex County Road 10 near Amherstburg on the east side of the Detroit River. Eight identical light traps were set up, extending linearly away from the lake or river and were operated simultaneously. Trap distances from the lake or river were 0, 78, 156, 312, 625, 1250, 2500 and 5000 m. Meteorological conditions were recorded to assess the effect of wind and temperature on dispersal abilities. Three dispersal experiments were conducted at each location. *Hexagenia* and Other Trichoptera were collected at Lake St Clair (17, 23, and 29 July 1987). *Hexagenia*, *Macronema* (Trichoptera) and Other Trichpotera occurred at the Detroit River site (31 July, 11 and 13 August 1987). Time and direction of arrival were recorded for all *Hexagenia* landing on the sheet.

Dispersal was assumed to be a random process, with distance travelled following a negative exponential model. Accordingly, mean dispersal distances were estimated by integrating the least squares regression curve relating Ln(catch) to distance from the lake or river. Additionally, estimated distance travelled by 50 percent and by 10 percent of the organisms was calculated according to the regression models. These distances were then taken to be the radius of a semicircle describing the area of lake or river from within which 50 or 90 percent of the animals originated.

RESULTS

Trap Efficiency

The light traps were effective for collecting large numbers of aquatic insects. Setup and operation of the traps was simple, requiring no special skills.

Samples collected in May and June 1987 have been sorted and identified. Two of the largest samples were split and stored at -20 and -70°C to determine if storage temperature has any appreciable effect on the results of the GC analysis.

Caddisfly and mayfly biomass (fresh weight) were plotted against time for the East Windsor and River Canard sites (Fig. 2), since adequate data are presently available for these sites only.

Single collections required an average of 2 kg of dry ice with a maximum of 3 kg on warm, humid nights (26°C, 80-90% RH). Since the traps were not air-tight, greater amounts were needed on windy nights. The CO_2 subliming from the dry ice quickly killed the insects entering the trap and also cooled the sample, preventing decomposition. Water condensation on the funnel and the vanes was noticeable only on especially humid nights, usually during the second hour of collection, by which time the number of insects entering the trap was significantly lower than during the previous hour. The lantern batteries used to power the light lasted for about 9 hours.

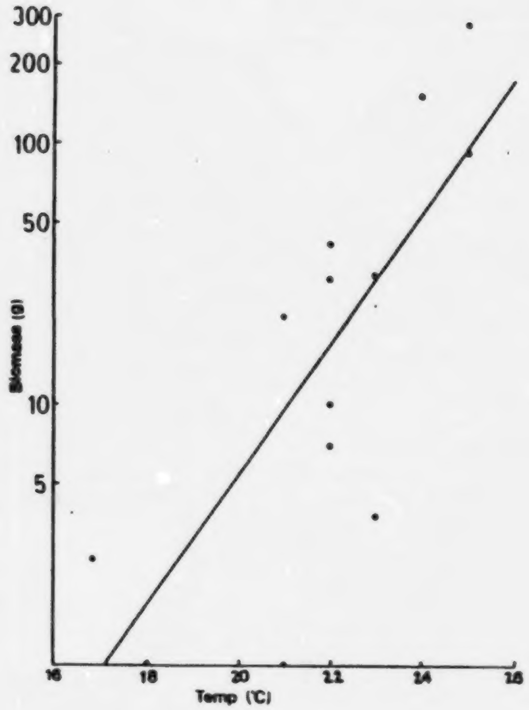

Figure 2. Relationship between temperature (°C) and catch of Trichoptera (g fresh weight) in light traps during June, 1987. Regression equation takes the form Ln(1 + Biomass) = 0.582(Temperature) - 9.96 ($R^2 = 0.59$, $p < 0.01$).

Ideal nights for collecting were warm, humid, and calm (wind velocity <10 kmh^{-1}). In June there was an exponential relationship between caddisfly activity and temperature (Fig 2, $R^2=0.59$ $p < 0.01$). Very few organisms were caught at temperatures below 20°C. Catches were usually reduced by the presence of other light sources, such as bright street lights, within 50 m of the light trap.

Best catches at all sampling stations were recorded at wind velocities <10 kmh^{-1}. At wind speeds >15 kmh^{-1} catches were greatly reduced, often to less than 100 insects. The light trap became susceptible to being blown over by gusts at wind velocities >20 kmh^{-1}.

Sample Composition

The River Canard sample station was located near a marshy area. Catches at this site were considerably more diverse than those at the other sites, which were located near rocky shores or breakwalls. Samples collected at the other sample sites contained mostly caddisflies and mayflies, requiring less sorting than those from the River Canard site.

Numbers of Caenis (Ephemeroptera) caught at the four stations were variable, and dependent on wind velocity and direction. This mayfly is small and shortlived, possessing limited dispersal abilities. In general, mayflies were more prone to being affected by the wind. At wind velocities >5 kmh^{-1} mayflies usually arrived with the wind. Below this wind velocity direction of arrival was not affected.

The taxonomic sequence of insects arriving at the trap can be described as follows: Mosquitoes (Culicidae) and Chironomidae were most abundant during the first 20-30 min of collection. Caddisflies exhibited greatest activity from 30-60 min past sunset, their numbers tapering off at the end of the first hour of collection. Incoming insect numbers were greatly reduced during the second hour of collection; only Coleoptera, and occasionally mayflies became more numerous. The arrival and peak activity time of mayflies was variable, ranging from the first ten minutes of collection to the last thirty minutes.

Seasonal variation

Collections at sample stations during most of May 1987 yielded very small samples, typically weighing less than 2 g (Table 2). The first larger sample (16 g) was collected on 26 May at the River Canard site. Thereafter, catches were larger, increasing steadily through June to the maximum weight collected on 23 June at both Detroit River sites (Fig. 3). Samples collected at the St Clair River sites were much smaller, and only started to increase towards the end of June.

Table 2. Sunset weather conditions and fresh weights of samples collected in May and June 1987. (DR = Detroit River, SCR = St. Clair River, U = upstream, D = Downstream, CLR = clear, OVC = overcast)

Date	River	Position	Temp. (°C)	Wind velocity (Kmh^{-1})	RH (%)	Cloud-cover	Trichoptera Biomass (g)	*Hexagenia* Biomass (g)	Total Biomass (g)
9 May	DR	D	14	0-2	49	CLR	0.0	0.0	0.0
19 May	DR	D	15	4-8	82	OVC	0.0	0.0	0.0
21 May	DR	U	34	3-6	76	OVC	0.0	0.0	0.0
26 May	DR	D	26	0-2	83	CLR	18.3	0.0	0.0
3 June	DR	U	22	4-8	40	CLR	41.65	0.0	44.0
8 June	DR	D	23	0-2	70	CLR	3.69	0.0	5.0
10 June	DR	U	17	0	53	CLR	2.54	0.0	4.0
11 June	SCR	D	21	0-2	60	OVC	0.0	0.0	0.0
11 June	SCR	U	18	20-25	60	OVC	0.0	0.0	0.0
15 June	DR	U	24	5-10	52	CLR	149.92	9.50	160.33
15 June	DR	D	22	2-5	52	CLR	31.60	0.9	35.0
23 June	DR	D	25	0	65	CLR	92.47	0.0	107.0
23 June	DR	U	25	0-5	65	CLR	280.3	259.0	567.3
24 June	SCR	U	22	0-5	58	CLR	7.0	27.1	35.0
24 June	SCR	D	22	0	58	CLR	10.1	21.5	35.9
30 June	DR	D	23	0-5	88	CLR	32.6	1.0	45.6
30 June	DR	U	21	0	88	OVC	23.5	0.0	25.0

Table 3. Results of regression analysis of dispersal data. Equations take the form Ln(1+Biomass) = a + b(Distance). (DR = Detroit River, SCR = St. Clair River)

	Regression statistics				$D_{0.5}$		$D_{0.1}$	
River	Taxon	Intercept (a)	Slope (b) (SE)	R^2	Dist (m)	Area (km^2)	Dist (m)	Area (km^2)
SCR	*Hexagenia*	4.101	-0.000529* (0.0001716)	0.83	1310	2.70	4163	27.2
SCR	*Hexagenia*	3.147	-0.000353** (0.0000714)	0.83	1963	6.05	6516	66.7
SCR	*Hexagenia*	2.125	0.000022 (0.0001061)	0.01	--	--	--	--
DR	*Hexagenia*	2.370	-0.000366* (0.0001732)	0.47	1893	5.63	6284	62.0
DR	*Hexagenia*	0.669	0.000083 (0.0001499)	0.06	--	--	--	--
DR	*Hexagenia*	1.353	-0.000354 (0.0001814)	0.43	1958	6.02	6504	66.5
DR	*Macronema*	4.981	-0.000331** (0.0000779)	0.78	2094	6.89	6948	75.8
DR	*Macronema*	2.526	-0.000339* (0.0001102)	0.66	2044	6.56	6785	72.3
DR	*Macronema*	2.326	-0.000583* (0.0001755)	0.69	1188	2.22	3950	24.5

* $p < 0.05$, ** $p < 0.01$

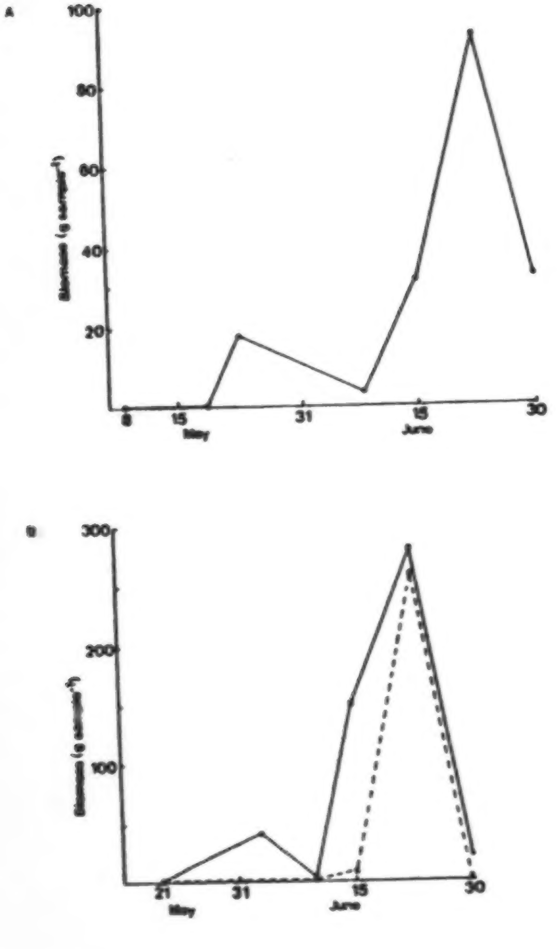

Figure 3. Seasonal variation in abundance of Trichoptera (solid lines) and Hexagenia (dashed line) in light traps, May and June, 1987. A, Detroit R. at East Windsor; B, Detroit R. at River Canard.

In general, caddisfly numbers showed a pronounced peak in late June, and declined through July and August. Mayfly numbers showed a similar pattern. However, the late June peak was much more pronounced. Samples collected along the St Clair river were considerably smaller throughout the collecting season than those from the Detroit River.

Collection of Uncontaminated Samples

Sampling in June near Balsam Lake provided adequate material for detection limit studies. Adults of Hydropsychidae (285 g) (Trichoptera) were collected at Horseshoe falls, near Minden, Ontario. Adults of *Hexagenia* (70 g) were collected at Balsam Lake, Rosedale, Ontario. The samples were sorted and stored at -70°C for detection limit studies to be performed later in the year. Biomass collected in early August in the same area was much reduced.

One sample was collected at the Ausable River, near Arkona, Ontario, on 17 August. This sample has not been sorted and is being stored at -20°C.

Dispersal Distance Studies

Results of dispersal distance studies are listed in Table 3. Relatively low numbers of *Hexagenia* and *Macronema* were the result of sampling late in the emergence season. Numbers of *Hexagenia* and *Macronema* were plotted against distance from the lake or river (Fig. 4). Points at 312 m (station 4) were excluded from the regression analyses because interference from bright streetlights greatly reduced the number of insects caught. Regression statistics for *Hexagenia* and *Macronema* are listed in Table 3. Three of six regressions for *Hexagenia* were non-significant. Although coefficients of determination for significant regressions were relatively high, significance was marginal owing to the relatively low number of data points. Estimates of distance travelled by one half of animals ($D_{0.5}$) or by only ten percent of animals ($D_{0.1}$) were calculated for all trials having an R^2 value of greater than 40% (Table 3).

Median dispersal distance estimates ranged from 1.3 to 2.0 km, suggesting that half of all animals caught originated within 2.7 to 6.0 km^2 of a shoreline trap. Ten percent or fewer *Hexagenia* dispersed 4.4-6.1 km; thus 90 percent originated within an area of 30-66 km^2. Distance estimates for *Macronema* indicate that this caddisfly has dispersal ability equivalent to or greater than that of *Hexagenia* (Table 3). Dispersal distances for other hydropsychid caddisflies have not yet been calculated. However, we estimate that other caddisflies travel only a small fraction as far as *Macronema*. *Macronema* is an exceptionally strong flyer among the Hydropsychidae (Ross 1944).

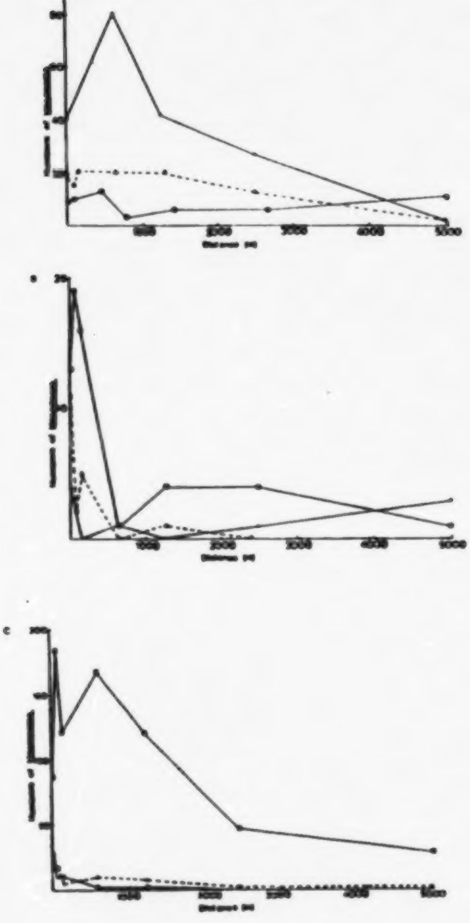

Figure 4. Relationship between catch of adult insects in light traps and distance inland from waterbody. Each curve represents collection on one night. Lines are drawn by eye through points. A, Hexagenia at Lake St. Clair near Belle River; B, Hexagenia at Detroit R. near Amherstburg; C, Macronema at Detroit R. near Amherstburg.

DISCUSSION

Relatively few studies have investigated the use of adult aquatic insects as biomonitors (Ciborowski and Corkum, In press). Our results indicate that adult Trichoptera and Ephemeroptera can be collected in large numbers using light traps. Samples are large enough to permit analysis by GC for organochlorine contaminants. The collecting equipment is relatively inexpensive, and requires no specialized skills to operate, as was proven during the dispersal studies where persons previously unfamiliar with the light traps were required to set up and operate them. The use of light traps to collect Trichoptera and Ephemeroptera yields larger numbers of insects with considerably less effort than the manual method used by Ciborowski and Corkum. However, light traps suffer from some of the same shortcomings as the manual method, namely that sizes of catches are greatly affected by environmental conditions, especially temperature and wind velocity. Catches were also reduced by the presence of bright lights nearby. Although the traps were most effective for Trichoptera, it is not known if all local genera of Trichoptera are equally attracted.

Most Trichoptera actively entered the traps and were available in sufficient numbers for unequivocal contaminant detection from June to mid-August, exhibiting peak numbers in late June. The extended availability of Trichoptera will allow evaluation of seasonal variability in contaminant concentration, which is scheduled for summer of 1988. The major factors affecting sizes of Trichoptera catches were temperature and wind velocity. Catches were larger on warm nights with wind velocities $<10\ \mathrm{kmh}^{-1}$, even near the end of the sampling season. Although detailed data are not available, relative humidity also seemed to influence catches; larger samples were collected on humid nights.

The traps were not successful in catching Ephemeroptera, which were attracted to the lights, but required hand collection. Mayfly numbers were low throughout the summer, exhibiting only one pronounced late June peak. Therefore, one should sample for mayflies at or near the peak emergence period to accumulate sufficient amounts of insects for analysis. Since *Hexagenia* were collected manually, our numbers reflect the actual mayfly density only for nights when incoming numbers were low enough for one person to collect all *Hexagenia* alighting on the sheet. Fortunately, this was the case during the dispersal distance studies. *Hexagenia* catches were also affected by the wind, due to the larger size and limited flight abilities of these insects. Slightly larger numbers were collected on calm nights, whereas catches were significantly reduced by windy conditions. Studies are scheduled for next summer to evaluate numbers of animals that will remain at unmanned traps.

Twice as many female *Hexagenia* as males were collected during the dispersal distance studies. Greater numbers of females than males were also observed in Trichoptera catches although exact numbers are not available at this point. Since the lipid content of females is greater than that of males due to larger body size and the high fat content of eggs, the results of GC analysis may be influenced by the predominance of females. While it is possible that females outnumber males in both Trichoptera and Ephemeroptera, trap selectivity may also account for the observed sex ratios.

Dispersal Distance Studies

The primary goal of our study is to demonstrate the utility of Trichoptera and Ephemeroptera as biomonitors. Therefore, it is important to delineate the area from which the samples are collected. Ideally, animals will come from a relatively small area surrounding the sample station. If animals disperse randomly, the number of animals decreases exponentially with distance from the source.

In our studies, the lake or river was considered to be the source of the insects collected. However, emerging mayflies and teneral caddisflies frequently move inland where they become sexually mature. Following, mating the females return to the water to oviposit. Therefore, greatest densities are expected at the water and/or some distance inland. Six of the plots in Figure 4 indicate an inland peak and three have peaks at the shore. The latter dispersal plots were based on very small samples, typically less than 30 insects per sample. Records of first appearance among dispersal sample sites also suggest that at least in some cases *Hexagenia* were returning from inland to the lake.

The median and 10 percent dispersal distances for *Hexagenia* and *Macronema* suggest that light trap catches represent a potentially large area around each of the sample sites. Although one-half of individuals are attracted from a relatively small area (2.5 to 7 km^2), 10 percent or more may arrive from an area encompassing up to 65 km^2. Animals that inhabit the midregions of large waterbodies must be strong fliers if they are to transform (from subimago to imago) or mate on land. Unfortunately, this may limit the utility of adults of these species as unequivocal indicators of sites of localized contamination. Alternative sampling designs, such as multisite trapping and triangulation of likely contaminant sources might be necessary to circumvent this problem if *Hexagenia* is to be an organism of choice. The magnitude of dispersal and their potential abundance suggests that animals carrying a high contaminant burden could be a significant source of loading to terrestrial habitats. We anticipate that dispersal distances of the smaller caddisflies are much less that those of *Macronema* and *Hexagenia*. Observations at the sample sites suggest that these insects do not disperse as far as *Macronema*.

It must also be noted that the dispersal distances measured apply primarily to inland dispersal. Caddisflies tend to disperse along rivers, especially upstream (Roos 1957), in which case our calculated inland dispersal distances may not be applicable. Further study is required to gain sufficient understanding of caddisfly dispersal patterns.

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RIVER MIXING ZONE

WHY

Predict water volume not achieving receiving water quality objectives for a specified river flow (e.g. 7Q10 etc).

WHEN

☐ New Discharge ☐ Use interference

☐ Change in discharge volume flow and/or quality

CAPABILITIES

Can quantitatively compare outfall locations and designs

Can quantify allowable discharge loadings

INPUTS

Receiving Water

☐ Flow ☐ Bathymetry ☐ Dispersion

☐ Water quality concentrations + temperature and pH

Effluent ☐ Flow ☐ Water quality concentrations

Outfall ☐ Location ☐ Diffuser design

OUTPUTS

Predicted two dimensional mixing zone

Predicted Critical Points

MIXING ZONES

Managing the Mixing Zones is an important component of any water quality management program. For toxic substances like total residual chlorine and ammonia which normally exceed the objectives in the discharge of treated waste water it is important to define the Mixing Zones, and examine different outfall diffusers and locations to reduce the size of the Mixing Zones.

A computer program has been developed to predict Mixing Zones. This model received the 1985 Wesley Horner Award of the American Society of Civil Engineering for the most valuable contribution to the Environmental Engineering Profession. The program uses locally measured river depth profiles, currents, dispersion, and receiving water background concentrations to predict the Mixing Zone. The program considers the decay of total residual chlorine and ammonia in the receiving water. Both nearshore and offshore diffuser outfalls can be considered.

The Mixing Zone program runs interactively on a personal computer with graphical calibration features. This enables the user to try different scenarios to reduce the Mixing Zone. There are four outputs from the Mixing Zone program. The first output summarizes all the input data in graphical form for each river cross section (see Figure 1). The second output is a two dimensional (across and downstream) concentration isopleth (see Figure 2). The third output is the same as the second, but in quasi three-dimensions (see Figure 3), and the fourth output defines the critical distance from shore to achieve a speciliced water quality objective (see Figure 4).

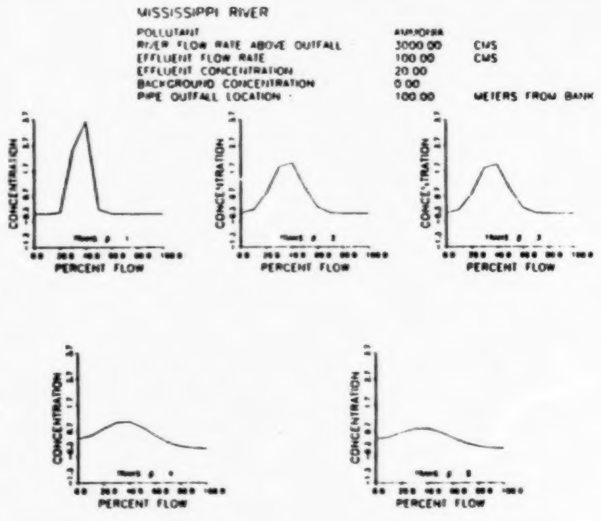

FIG. 1

Uses of Mixing Zone Program

A Mixing Zone study can be used to define the allowable loadings for a discharge, either by regulation on the allowable size of the Mixing Zone or interference with other water uses. The study can also determine the preferred location and type of outfall to minimize the impact on the receiving water.

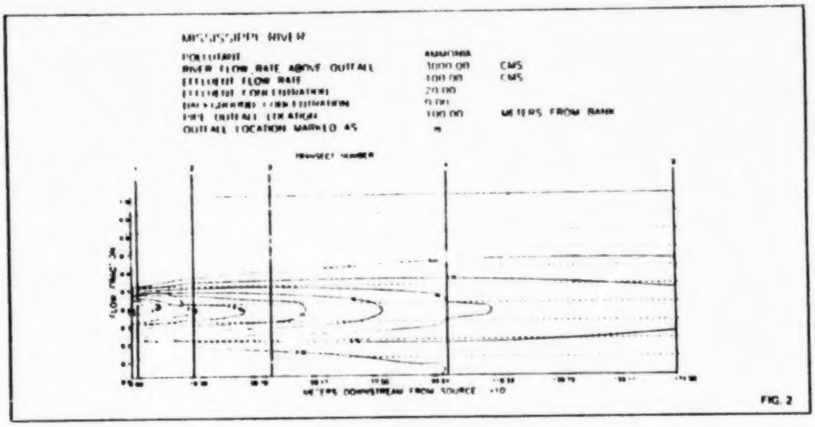

FIG. 2

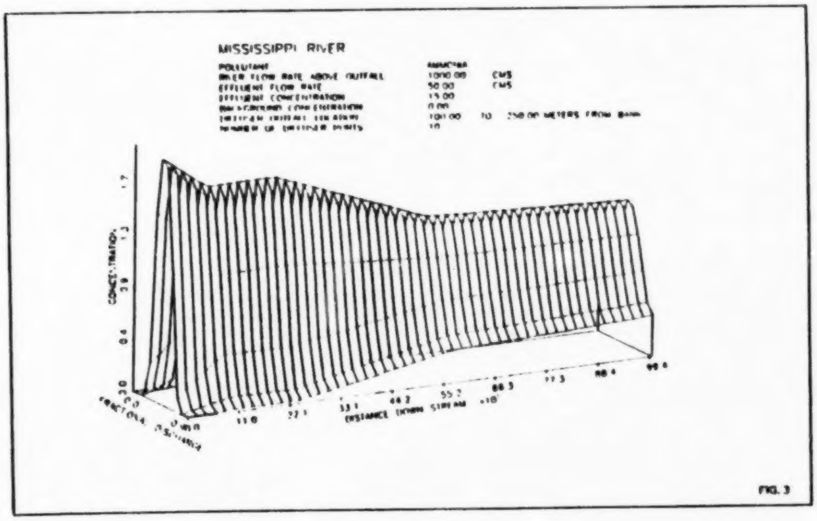

FIG. 3

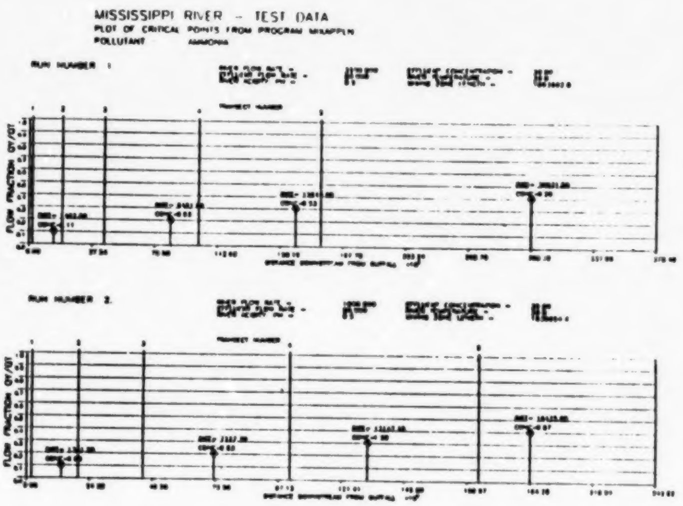

FIG. 4

SERVICES AVAILABLE

Total Services

We will carry out the necessary field studies, and using the Mixing Zone program examine alternatives in discharge loadings and outfall location and design for compliance with the guidelines and objectives of the regulating authority. The alternatives will be discussed in a report and recommendations made with respect of loadings, outfall location and design.

Partial Service

To reduce the costs of the study a client may wish to use its own resources. If the client has field staff available we can instruct the field staff on the data required and lease equipment if required. If the client has water quality and computer staff, we can provide instruction on the use of the Mixing Zone programs and the client may perform the planning evaluations.

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A Convenient "Macro" Programme for the Quantification of PCBs in Environmental Samples

by

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Because there are many congeners in PCBs, the quantitative analysis of Aroclors by gas chromatography is made difficult because of the large number of peaks that appear in the chromatograph. Separation of the congeners on a capillary column and detection with an electron-capture detector reveals dozens of peaks. Because the electron-capture detector is not able unambiguously to identify PCB congeners, a careful selection of oven programme must be made such that the elution times are optimized for PCBs. A careful selection of peaks for quantitation must be made such that the intensity of the peaks will allow for their quantitation at low concentrations. From the sixty or more peaks separated on a Hewlett-Packard Ultra capillary column coated with cross-linked phenyl silicone, eighteen were chosen for quantification.

Calibration and Macro programmes were written for the Hewlett-Packard 5895 Workstation. The standards were chosen to bracket the expected concentrations in the samples. Responses from the chosen peaks were averaged and the response factor updated for each standard. A linear calibration curve is achieved for the standards with a non-zero intercept. Analyses of quality assurance samples provided by the MOE laboratories in Rexdale gave satisfactory analyses for PCBs. Also, spiked fish samples were extracted following MOE protocols and gave excellent recoveries of PCB spikes.

Although chlorinated pesticides can be separated satisfactorily from PCBs by column chromatography, hydrocarbons pose a problem. Thus, the organic fraction from the extraction of some sediments and road oils may contain predominantly hydrocarbons. In these situations, gas chromatography with electron-capture detection may be unsatisfactory for the analysis of PCBs. In these cases, gas chromatography-mass spectrometry can be used to determine PCBs. The Selected Ion Monitoring mode (SIM) provides an unequivocal identification of PCB congeners. Again a selection of peaks is made on which to quantify. Congeners are identified by a choice of peaks from the mass spectrum of the standard. Two of the peaks from the mass spectrum are used as qualifiers, with a range of responses relative to the quantifying ion. Failure of the qualifiers to meet the target values results in the peak's being flagged, with an indication that the qualifiers were not satisfied. A drawback of the GC/MS is that the quantification limit is considerably higher than in the case of GC/ECD.

PROJECT NO. 203 PL

EFFECTS OF RURAL AND SUBURBAN DEVELOPMENT ON SURFACE WATER QUALITY
IN FIVE SELECTED SUB-WATERSHEDS IN
THE UPPER HUMBER RIVER

INTRODUCTION

The Humber River drainage area of 857 km^2 is the largest watershed under the jurisdiction of the Metropolitan Toronto and Region Conservation Authority encompassing about one-third of the total area within the Authority. The southern portion of the watershed, within the Metropolitan Toronto boundaries is heavily urbanized. North of Metro, within the Regional Municipalities of Peel and York, the watershed is predominantly rural (Figure 1).

Previous research on the Humber River (TAWMS, 1984, 1985; Hindley et al 1986) indicated widespread pollution occurring within this watershed, from both point-source urban inputs as well as diffuse-source inputs.

The purpose of this study was to assess in greater detail the relative pollutant contributions from five of the most predominant land use sources within the watershed: construction activity, agricultural row crops, livestock access, streambank erosion and undisturbed forest.

METHODS

The five study sub-watersheds ranged in size from 2.6 ha to 21.9 ha and were all located in the northeastern portion of the Humber River watershed. The main criteria used in selecting candidate sub-watersheds were as follows:

1. Ideally, all sub-watersheds should be in reasonably close proximity to one another.

2. All sub-watersheds should be influenced, as much as possible, by the one land use of interest (i.e., there should be no unrelated point sources discharging within the basin).

3. Ideally, all watersheds should be selected on streams which are not intermittent but maintain a reasonably consistent year-round flow.

Surface water samples, under dry, wet, and springmelt conditions were collected at stations immediately upstream and downstream of each land use area, eliminating as much as possible any extraneous inputs. Bed sediment and soil samples were also collected on occasion and bed load samples and off-stream sediment traps installed.

RESULTS

Preliminary results are described for the individual study watersheds.

Livestock Access Site

Substantial differences were observed in geometric mean fecal coliform concentrations between the upstream and downstream sampling stations under both dry and wet weather sampling periods. In dry weather, the mean upstream FC density was about 15/100 ml increasing at the downstream station to 1995/100 ml.

Wet weather FC densities ranged from 38 to 400/100 ml (geo. mean = 149/100 ml) at the upstream station and from 2,000 to 660,000/100 ml at the downstream station (geo. mean = 29,000/100 ml). Fecal coliform densities during the springmelt sampling were well below the MOE objective and few upstream/downstream differences were observed.

The greatest fecal coliform concentrations occurred while cattle accessed the watercourse and were due to instream defecations and disturbance of the stream bottom. Some efforts were also expended in investigating the potential for streambed sediments to act as bacterial reservoirs. Bacterial analyses performed on two water column and bottom sediment samples from each station indicated much greater E. coli concentrations within the bottom sediments compared to the overlying water. Within the sediments, E. coli concentrations were greatest in samples collected within the first one cm of sediment, compared to samples collected at the two to three cm depth. Overall, the greatest concentrations occurred in shallow sediments collected at the downstream station, where E. coli densities were about 500 times greater than in the overlying water.

Agricultural Site

Few parameters displayed marked increases in concentration between the upstream and downstream stations under any weather conditions. Most parameter concentrations were within established guidelines or objectives.

Sediment traps installed around the perimeter of the corn field prior to two storm events indicated a great deal of soil movement had occurred. Some traps were covered by up to 10 cm of soil after the second event. Upstream and downstream total suspended solids and turbidity measurements however, did not reflect this soil movement, probably for two reasons. The soil movement which appeared evident from the sediment traps may not have resulted in significant transport into the watercourse. Also of likely importance was a considerable widening of the stream channel in the vicinity of the downstream station and a corresponding decrease in stream velocity which may have resulted in deposition of suspended material upstream of the sampling site.

Construction Site

Instream parameter levels generally did not differ greatly between the upstream and downstream sampling stations. The most obvious differences occurred during wet weather sampling, when the mean total suspended solids concentration increased from 56 to 305 mg/l at the upstream and downstream station, respectively.

Sediment traps installed at runoff channels leading from the construction site suggested significant sediment movement still appeared to occur from this site despite the completion of the majority of construction activities. Although newly generated sediment was likely transported during these events, visual observation suggested the majority of movement occurred from sediments which were disturbed during the initial cleaning phase. Soil cores, collected along transects adjacent to the watercourse indicated the soil displaced during construction had been transported over a much greater area than was initially evident. Volume estimates, based upon the cores, suggest several hundred m^3 of fine to medium sands had been displaced from the construction site.

Streambank Erosion Site

Very few obvious changes in parameter concentrations were noted between the upstream and downstream stations. When changes did occur, there was difficulty in ascribing them to streambank sources. The width of the Humber River at this location and the relatively large volume of water made it difficult to accurately monitor changes in water quality by grab sampling. Bridge construction which occurred immediately upstream of the study area also likely contributed to the difficulties by masking sediment input from the erosion sites.

Detailed bank profile measurements of a slumping section of streambank erosion yielded mixed results. Subsequent remeasuring of the bank at one and two year intervals indicated soil loss of 196 and 168 m^3, respectively.

Control Site

Surprisingly high bacterial densities in dry weather samples at this site prompted more intensive monitoring. Fecal coliform densities of 1000 cts/100 ml at the upstream site suggested the possibility of groundwater contamination since the water exited the ground just 25 metres above this point. In water samples collected near the source, fecal coliform densities were well above the MOE objective. Possible sources of bacterial contamination were identified and are discussed in the report.

CONCLUSION

The use of small sub-watersheds with homogeneous land uses yielded mixed results. While their size virtually eliminated extraneous inputs to the study area, the generally small watershed area and short watercourse length made it difficult, particuarly during dry event and springmelt sampling, to detect appreciable changes in parameter concentrations between the upstream and downstream stations.

The greatest bacterial impacts were observed within the livestock sub-watershed. The daily watering of cattle within the stream and their associated fecal inputs caused severe contamination of downstream water. The significantly greater bacterial concentrations within the streambed sediments vs. the water column suggests that downstream impacts from fecal contamination may be felt long after the cattle have been removed from the stream.

These and other conclusions are further elaborated upon in the report.

An Ecosystem Approach to Monitoring PCB's in Pristine Ontario Lakes

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A three year study was started in 1986 to ascertain the significance of atmospheric deposition in determining the level of PCB's in the biota of Ontario Lakes. It has been estimated that 7.5 µg to 24 µg (Swackhamer and Armstrong 1986, Murphy and Schinsky 1983, respectively) of PCB's are deposited per square meter per year from the atmosphere into the lakes in the Great Lakes region. This particular source may account for up to 80% of the PCB's entering the Great Lakes (Thomann and Di Toro 1983) and will probably be the major input into isolated lakes. Because of their highly lipophilic nature (Kow of 105 to 109), PCB's tend to accumulate within the organic components of the lake system, such as the lipids of biota or the organic fraction of particulates and sediment. In addition, they do not degrade rapidly, so the sediment, particulates and biota provide a record of the current and past lodes of PCB's entering the lake. It is the objective of the present study to survey the levels of PCB's in the environmental compartments of seven Ontario lakes to provide estimates of the rates of input of organic contaminants and also the pathways of movement through each lake ecosystem. Estimates of atmospheric input will be made by modelling of the lake system using environmental fate models (EXAMS2, WASP4 and WASTOX) developed by the U.S. Environmental Protection Agency.

Selection of the lakes for intensive study was based upon their trophic status, degree of isolation and the level of contamination in the biota. The lakes were divided into low (<10 ppb wet weight in smallmouth bass), medium (10-100 ppb) and high (>100 ppb) levels of contamination based on monitoring conducted by the Ontario Ministry of the Environment. The study lakes included Scugog and Wood (low contamination); Boshkung, St. Nora and Bark (medium); Rice and Clear (high). In 1987, Bark Lake was removed from the study and Opeongo Lake added to increase the number of isolated, uncontaminated lakes.

Samples of sediments, zooplankton, crayfish, anodontid clams and 5 species of fish were collected in late 1986 and in the spring of 1987. Sediment cores were collected from the deepest deposition zone of each lake using a KB corer. The upper 9 cm of each core was divided into three fractions of 0-3, 3-6 and 6-9 cm for PCB analysis. Separate sediments samples were analysed for organic content and particle size distribution. The concentration of dissolved PCB's in lake water was measured by filtering 18 L of water through 0.30 µm Millipore filters and extracting the filtrate with 1 L of dichlormethane. The filters were extracted separately to give the concentration of PCB's in the suspended particulate fraction.

Where possible, samples of biota were collected in well-mixed zones within each lake to avoid dilution or contamination from input streams. Zooplankton were collected using a 0.5 m2 conical net towed for 5 minutes at a depth of 5-10 m in the deepest area of each lake. Invertebrates, crayfish and clams were collected by dip net along the shoreline and in the littoral zone. Fish were collected by seine net, trap net and by angling. Fish species collected were golden shiner (*Notemigonus crysoleucas*), bluntnose minnow (*Pimephales promelas*), yellow perch (*Perca flavescens*), smallmouth bass (*Micropterus dolomieui*) and lake trout (*Salvelinus namaycush*). A range of body sizes of each fish species was collected in order to determine any relationships between PCB concentration and size. Samples of muscle from the mid-dorsal region of each fish and from the tail of crayfish were used for analysis while whole body was analysed in clams and invertebrates. Extracts from water, sediments, suspended particulates and biota were analysed for 21 PCB congeners and DDT using a Varian 3500 gas chromatograph with 30 m DB-5 capillary column and EC detector.

Preliminary analysis of data supports the original data from OME used for the selection of the study lakes. The concentration of total PCB's (i.e. the sum of all 21 congeners) in yellow perch ranges from a minimum of approximately 9.6 ng g-1 (SD=3.9, n=5) wet weight in Wood Lake to 39 ng g-1 (SD=21, n=11) in Rice Lake and 90.8 ng g-1 (SD=45, n=10) in Lake Clear. The same trend is observed for golden shiner, bluntnose minnow, crayfish, smallmouth bass and lake trout. The baseline levels of PCB's in the biota of uncontaminated lakes is approximately 7-10 ng g-1, with little variation due size or trophic status. The maximum value for smallmouth bass was in Lake St. Nora (41.1 ng g-1, SD=21.3, n=5) while the highest concentration for trout was in Lake Clear (2900 ng g-1 (n=1). In all lakes where lake trout were collected, they contained the highest concentrations of PCB's found in the biota. Analysis of biota samples is continuing in order to expand sample sizes for statistical comparisons between and within lakes.

There are differences in the composition of PCB's found in the biota of the individual lakes. The biota of Wood Lake and Scugog Lake have a higher percentage of lower chlorinated congeners (PCB 18 and 52), while Rice Lake and Lake Clear show a wider range of congeners; but predominantly the higher chlorinated compounds such as PCB 118/149 and 138. These latter congeners are present in Aroclor mixtures 1254 and 1260. In addition, lake trout appear to contain a different pattern of PCB congeners than the biota in the lower part of the food web within the same lake.

Some preliminary data are available for a wide range of samples from Lake Clear, an oligotrophic lake in Renfrew county that was accidently contaminated with PCB's in the mid-1970's. Perch, zooplankton, crayfish and invertebrates contain approximately 60-90 ng g-1 PCB's; the highest of all the lakes studied. A single lake trout collected in 1986 had a concentration of 2900 ng g-1 wet weight in muscle. The upper fraction of sediment (0-3 cm) had approximately 580 ng g-1 (SD=170, n=5) dry weight but the concentration decreased to 260 ng g-1 (SD=43, n=5) at a depth of 6-9 cm. This indicates that the upper layer of sediment may be well mixed with the water column, and PCB's may be returning to the food web despite a relatively high organic content in the sediments (ca. 11%). There was no evidence of dechlorination of the higher chlorinated congeners in the sediments, as suggested by Brown et al. (1987), since the pattern of congeners is consistent at all levels of the sediment profile and was identical to that of the biota. These data from Lake Clear will be used to standardize the mathematical models which will then be applied to the other test lakes.

Our immediate objective is to build up a full set of data for sediments, water and biota and to develop models for transport processes within each of the study lakes. It is predicted that food web transfer of the PCB's should be similar between lakes, but that other transport processes, such as particulate transport, will vary with lake morphometry and trophic status of the lake.

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